

PRESENT-DAY THEORY OF CHAIN REACTIONS

V. N. KONDRAT'EV

Institute of Chemical Physics, Academy of Sciences, U.S.S.R.

Usp. Fiz. Nauk 88, 769-781 (April, 1966)

1. RADICAL, OR CHEMICAL, CHAINS

CHEMICAL chain reactions were discovered in 1913 by M. Bodenstein^[1] who established that the quantum yields of a number of photochemical reactions are very large. Since according to the Stark-Einstein^[2] photochemical law no more than 1-2 molecules should react for each absorbed quantum, Bodenstein concluded that the primary photochemical act is followed by a long chain of chemical transformations, in which a large number of molecules of the initial substances take part, a fact which determines the magnitude of the quantum yield.

Of decisive significance for the further development of the chain theory of chemical reactions was the mechanism proposed by W. Nernst^[3] to explain the reaction of chlorine and hydrogen, discovered and subsequently investigated in detail by Bodenstein. According to Nernst's mechanism, which has long since become generally accepted, the active centers of this reaction are free chlorine and hydrogen atoms, i.e., valence-unsaturated particles which appear during the course of the reaction.

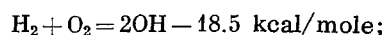
The following important stage in the development of chain theory was the discovery of branched chain reactions by N. N. Semenov and K. Hinshelwood.* The theory of branched chain reactions was first most clearly formulated in an article by Semenov^[5] and subsequently in his book "Chain Reactions."^[4]

According to this theory a branched chain reaction occurs in the following elementary stages: initiation, continuation, branching, and breaking of chains.

The enormous number of investigations carried out since the discovery of branched chain reactions up to the present has shown convincingly that both simple and branched chain reactions occur through the agency of valence-unsaturated particles—radicals, as assumed by Nernst in the instance of the reaction of chlorine with hydrogen. For this reason the chain reaction mechanism is usually referred to as the radical, or chemical, mechanism. From the point of view of this mechanism the initiation of chains consists of the process of production of free radicals (in particular, atoms) by a thermal, catalytic, photochemical, or other process. In the course of the continuation of the chains the monoradical which entered into the reaction is replaced by another monoradical, this being ensured

by the law of conservation of valence in processes of this type. Unlike this, the branching of a radical chain is always connected with an increase in the free valence, when, for example, three new monoradicals appear instead of the one which entered into the reaction. Finally, the breaking of chains occurs when the radicals recombine, join some molecule and form an inactive particle, or are adsorbed on a wall.

The oxidation (combustion) reaction of hydrogen which has been studied in greatest detail can serve as an example of a branched chain reaction. The initiation of chains can in this case be due to the homogeneous process

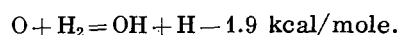


there are, however, grounds for assuming that the chains in the oxidation reaction of hydrogen are initiated on the walls of the reaction vessel.^[6] The initiation of chains is the slowest process because of its very endothermic nature and is the reason for the fact that noncatalytic oxidation of hydrogen occurs only at elevated temperatures ($T > 700^\circ\text{K}$).

The next in order of difficulty of occurrence is the branching process

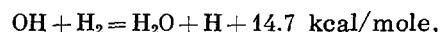


which is followed by the fast process



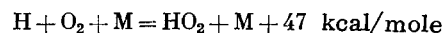
As a result of the first of these processes there appear in place of the H monoradical the monoradical OH and the biradical O which reacts with H₂ and is "changed" into two monoradicals OH and H. Thus, two additional monoradicals are formed as a result of both of these processes at the price of a loss of $16.6 + 1.9 = 18.5$ kcal/mole, i.e., the free valence increases by two units.

In this reaction the chain is continued by the process



whose rate determines the total reaction rate.

Finally, the breaking of chains in the absence of impurities at low pressures (mm Hg) is determined by the adsorption of active (H, O, OH) centers on the walls of the reaction vessel, and at pressures of tens of mm Hg and above by the process



(M is an arbitrary particle), as a result of which the very active H atom is transformed into the low-activity HO₂ radical.

*For references see the book "Chain Reaction"^[4] by N. N. Semenov.

A characteristic feature of the branched chain reactions is the occurrence of "inflammability limits." Thus, in the case of rich H_2-O_2 mixtures, for example, when the breaking of chains is due mainly to adsorption of H atoms, the condition for the inflammation of the mixture can be written in the form

$$\frac{d(H)}{dt} \gg 0.$$

Assuming stationary concentrations of O and OH, i.e.,

$$\frac{d(O)}{dt} = 0, \quad \frac{d(OH)}{dt} = 0,$$

and neglecting the rate of chain initiation, the condition for the inflammability limits

$$\frac{d(H)}{dt} = 0$$

can in the kinetic region be written in the form

$$p^2 - 2ap + b = 0,$$

where a is the ratio of the rate constants of the branching process $H + O_2 = OH + O$ and of the process of volume breaking of chains $H + O_2 + M = HO_2 + M$, and b is the ratio of the reaction constants of heterogeneous and homogeneous chain breaking multiplied by the ratio of the total pressure of the mixture to the partial pressure of the oxygen. Both a and b are functions of the temperature. Generally speaking we thus obtain from the preceding quadratic equation for each temperature two limiting pressures: p_1 (the lower, or first limit) and p_2 (the upper, or second limit). At a given temperature, inflammation is possible only at pressures satisfying the condition

$$p_1 \leq p \leq p_2.$$

The temperature dependence of p_1 and p_2 is such that on lowering the temperature they tend to a common limit a . We have thus on the pT diagram a characteristic inflammation peninsula. The cape of this peninsula corresponds to a pressure $p = a$ and a temperature given by the condition $a^2 = b$.

A third inflammability limit, characterized by a pressure $p_3 \gg p_1, p_2$, is observed at higher pressures. The inflammation condition at the third limit is generally determined by the circumstance that as a result of the increased pressure of the mixture the reaction rate is such that the released heat has no time to be carried away. This leads to a fast increase of the temperature and to inflammation of the mixture. Inflammation at the third limit has therefore been called thermal inflammation or an explosion. (Figs. 1-3).

However, inflammation of hydrogen-oxygen mixtures at the third limit is also possible under isothermal conditions^[7] (similar in this respect to inflammation at the first and second limit). In this case inflammation is due to the transformation of the little-active HO_2 radical into the active H and OH radicals in the processes^[8]

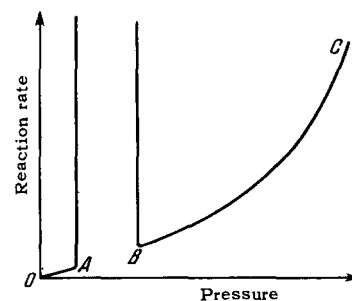


FIG. 1. Inflammability limits of a mixture of hydrogen and oxygen (with respect to pressure) at constant temperature.^[36]

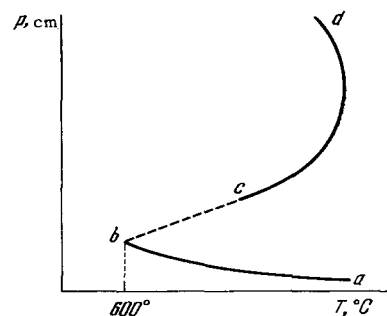


FIG. 2. Three inflammability limits of a $H_2 + O_2$ mixture according to^[37] (section ab based on data from^[38] and^[39], section cd based on^[40]).

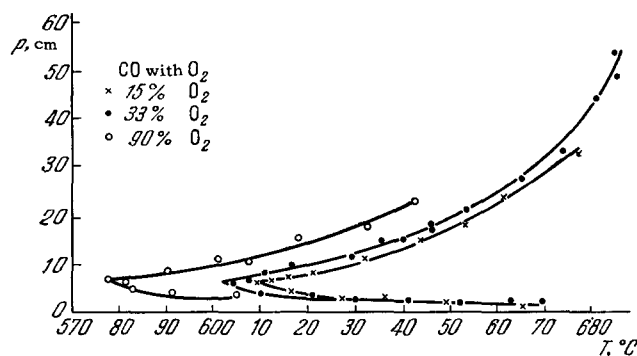
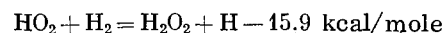
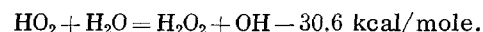


FIG. 3. Inflammability limits of CO and O_2 mixtures.^[37]



and



The occurrence of three (pressure) inflammability limits is a characteristic feature of the branched chain reactions. Unlike in the case of the latter, when there is no branching (simple chain) only one inflammability limit is observed; this limit is thermal. The reaction of chlorine with hydrogen can serve as an example of such a reaction.

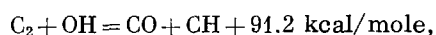
Together with discovering branched chain reactions, Semenov worked out the theory of heterogeneous breaking of chains, the theory of inflammability limits, and the theory of chain and thermal explosion.^[4] This was a remarkable contribution to the study of the chemical

process, whose theoretical significance and exclusively large importance for practical applications it is difficult to overestimate.

2. ENERGY EXCHANGE IN THE CHEMICAL REACTION OF MOLECULES

In the theory of radical chain reactions it is implicitly assumed that all reacting particles have an equilibrium energy distribution over all the degrees of freedom. However, any chemical reaction is unavoidably connected with a disturbance of the equilibrium energy distribution, which can be due to two factors. The first of these consists of a decrease in the concentration of the most energy-rich molecules which are used up in the reaction. This factor is most clearly evident in endothermic processes, in particular in processes of thermal dissociation of molecules. The second factor leading to disturbance of the equilibrium energy distribution in the course of a chemical reaction is the energy released in exothermic processes; this energy is distributed among the molecules of the products of the exothermic processes. Bearing in mind exothermic chemical reactions, which include practically all chain reactions, we will confine our discussion below to the influence of this second factor only on the kinetics and mechanism of the chain reaction.

Many direct experimental data are known at present which allow us to draw conclusions about the nature of the primary energy distribution in the products of exothermic processes. Thus, for example, measurements^[9] of the "translational temperature" from the Doppler broadening of emission lines of the CH radical in rarefied oxygen flames of acetylene produced in the process

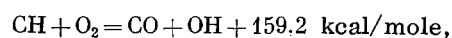


yielded 4000°K, whereas the theoretical maximum temperature of the flame is 2500–2800°K. One can conclude from this that electronically excited CH radicals* appearing in the acetylene flame have an energy of translational motion which exceeds the average thermal energy approximately by a factor of 1.5.

Measurements of the intensity distribution of rotational lines in emission or absorption spectra of flames indicate, further, that the rotational energy of the particles appearing in exothermic processes often also exceeds appreciably the average thermal energy. Since the measured intensity distribution usually corresponds to a Boltzmann distribution, it is possible to characterize the rotational energy of the molecules by their "rotational temperature." As an example we take the "rotational temperature" of the hydroxyl in the emission spectrum of acetylene-oxygen flames. The rotational temperature of electron-excited hydroxyl,† appearing apparently in the process

*Excitation energy 66.2 and 74.2 kcal/mole.

†Excitation energy 93.4 kcal/mole.

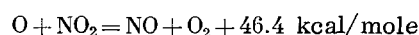


measured by Gaydon and Wolfhard^[10] for various pressures of the mixture (from 1 atm to 1.5 mm Hg) turned out to increase with decreasing pressure from 5400°K at 1 atm to 8750°K at 1.5 mm Hg (the maximum flame temperature at 1 atm is 3400°K); for smaller pressures it is correspondingly lower).

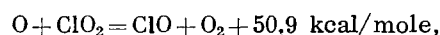
Taking into account the rotational-energy exchange in collisions of the hydroxyl with other molecules, as well as the quenching of the chemiluminescence, one can show that the energy corresponding to the maximum "rotational temperature" should be close to the rotational energy of the excited hydroxyl at the instant at which it is produced. This energy (proportional to the "rotational temperature") turns out thus to exceed by a factor of three and more the average rotational energy of the OH at the flame temperature.

Spectroscopic investigations of flames indicate that the vibrational energy of the molecules in the reaction zone often also exceeds the equilibrium energy at the flame temperature. Thus, for example, measurements of the relative intensity of the hydroxyl bands corresponding to $v' = 0, 1,$ and 2 (v' is the vibrational quantum number of the upper state) in the emission spectrum of a rarefied hydrogen flame^[11] yielded values corresponding to the intensity at 9000°K (the flame temperature was 1000°K).

A graphic proof of the excitation of high vibrational levels in the course of a chemical reaction is provided by investigations of absorption spectra and also of rotational-vibrational emission spectra of newly produced molecules. Thus, for example, in the absorption spectrum of molecular oxygen produced in the reactions

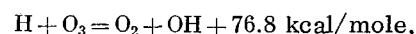


and



Norrish and co-workers^[12] observed intense bands due to transitions from vibrational levels $v'' = 4, 5, 6, 7,$ and 8 which are not observed under normal conditions because of the negligibly small number of O_2 molecules in these states. It follows from these data that the vibrational energy per O_2 molecule produced according to the above processes can reach 74 and 67 percent respectively of the heat of reaction.

An even larger amount of energy in the form of vibrations is carried off by the hydroxyl molecule produced in the process



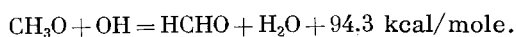
This reaction was first used^[13] to explain the origin of the rotational-vibrational emission bands of hydroxyl observed in the spectrum of the night sky.^[14] Subsequently these bands were also observed in the reaction of H atoms with ozone under laboratory conditions.^[15] Both in the spectrum of the night sky and under labora-

tory conditions bands are observed which correspond to transitions from the level with $v'' = 9$ and lower levels; it follows hence that the OH molecules appearing in the $H + O_3 = O_2 + OH$ process have a vibrational energy reaching 75.0 kcal/mole ($v'' = 9$), i.e., 98 per cent of the heat of reaction.

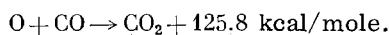
In a large number of cases one observes in the chemiluminescence spectrum, along with the rotational-vibrational bands, bands and lines due to the electronic excitation of the reaction products, and intermediate substances which indicate the appearance of electronically excited particles in the course of the reaction. We have mentioned above the electronically excited CH and OH radicals observed in acetylene flames. Let us also cite the following example.

In the reaction of H atoms with ozone at a pressure of several mm Hg, one observes in addition to the above-mentioned rotational-vibrational OH bands, O_2 bands due to the electronic transition ${}^1\Sigma_g^+ - {}^3\Sigma_g^-$.^[16] The electronically excited O_2 molecule (excitation energy 37.7 kcal/mole) appears here in the $H + O_3 = O_2 + OH$ process.

Characteristic of the spectrum of cool flames is the emission of electron bands of formaldehyde, whose excitation energy is about 80 kcal/mole. As was recently shown by Shlyapintokh et al.,^[17] the process which gives rise to the excitation of these bands is



We shall still mention the spectrum of the flame of carbon dioxide which includes bands of electronically excited CO_2 molecules appearing in the process



Measurements of the absolute intensity of the spectrum of an oxygen flame burning at a pressure of about 100 mm Hg and a temperature of about 1000°K^[18] showed that under these conditions one excited molecule of CO_2 is produced for each 125 molecules. The measured intensity is immeasurably larger than the intensity of the equilibrium emission at the flame temperature, a circumstance which is directly related to the nonequilibrium concentration of O atoms in the flame which exceeds by a factor of thousands their equilibrium concentration.

Molecules which possess excess energy naturally enter more easily into chemical reactions compared with molecules whose energy is equal to the average thermal energy. This is borne out by the numerous cases of the appearance of "hot" particles in photochemical reactions. We shall confine ourselves here only to the following example. In the photodisintegration of CH_3I by the 2537 Å mercury line "hot" CH_3 radicals appear; this follows from the fact that (in the temperature range 40 to 100°C) the rate of production of methane in this reaction is independent of the temperature.^[19] Indeed, since the process



responsible for the production of methane under the given conditions, has in the case of "cold" CH_3 an activation energy of about 10 kcal/mole,^[20] one would expect on increasing the temperature from 40 to 100°C a more than tenfold increase in the rate of production of CH_4 . The fact that the rate of production of CH_4 is independent of the temperature is consequently evidence of the fact that "hot" CH_3 radicals, considerably more active than the usual radicals, are produced in the photochemical reaction.

From all that has been said it follows clearly that the assumption of an equilibrium energy distribution in the reacting system, excluding participation in the reaction of energy-rich ("hot") particles produced in the exothermic links of the reaction, can, generally speaking, be considered valid only in instances when the reaction time (calculated per particle) exceeds the time of thermal relaxation. If, on the other hand, the latter cannot keep up with the reaction, energy-rich particles, which may have a considerable effect on the kinetics and mechanism of the reaction, accumulate in the reacting system. The role of this energy factor is most clearly manifested in the so-called energy chains.

3. RADICAL-ENERGY CHAINS

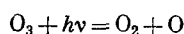
Bodenstein^[21] was the first (in 1916) to use the energy factor to explain the chain character of the photochemical reaction of chlorine and hydrogen. He assumed that the electronically excited chlorine molecules are the primary active centers of this reaction: reacting with the hydrogen molecules, they produce excited molecules of the reaction product HCl, which colliding with the chlorine molecules can impart to them their energy, as a result of which there occurs a regeneration of active (excited) chlorine molecules. However, the energy mechanism proposed by Bodenstein for the reaction of chlorine with hydrogen turned out not to be sound, since it contradicted spectroscopic data, and was replaced by the radical mechanism proposed by Nernst.

The concept that the active reaction centers are energy-rich valence-saturated molecules is also encountered in the work of Christiansen and Kramers^[22]; they attempted to apply chain concepts in order to explain the large rate of monomolecular reactions. Christiansen and Kramers assumed that the reaction products which have excess energy can transfer this energy to the molecules of the initial substance: as a result there appear new active molecules and the reaction develops in chain-like fashion (energy chain). However, the concept of energy chains was not confirmed in the subsequent development of chemical kinetics.

Only comparatively recently has the question about

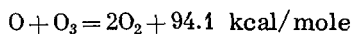
energy chains again been raised^[23] in connection with the increased interest in chain reactions at high temperatures for which the reacting system contains large amounts of energy and the resulting large concentrations of energy-rich particles. However, since a high temperature also favors the dissociation of molecules into free atoms and radicals, one should above all expect two factors to be important for the development of chains under high-temperature conditions: an energy factor and a chemical, or radical, factor. In other words, at temperatures when the thermal relaxation time is larger than the reaction time (calculated per elementary act) mixed radical-energy chains must be considered most probable.

Until recently the only example of such reactions was the photochemical dissociation of ozone by ultraviolet light ($\lambda < 2500 \text{ \AA}$). In this case there appears in the primary chemical act

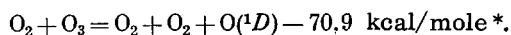


an electronically excited (metastable) oxygen atom in the ^1D state (excitation energy 45.4 kcal/g-atom). Indeed the participation and regeneration of the $\text{O}(^1\text{D})$ atom is used to explain the fact that the quantum yield of this reaction reaches^[24] a value of 8, whereas the photochemical reaction of ozone in visible (orange) light in which there appear in the primary act oxygen atoms in the ground state (^3P) occurs with a quantum yield of 2.^[25]

In the interaction of the $\text{O}(^1\text{D})$ atom with an ozone molecule according to the scheme

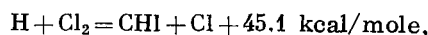


94.1 + 45.4 = 139.5 kcal/mole are released, i.e., on the average 70 kcal/mole for each oxygen molecule. This energy is sufficient for the continuation of the chain reaction



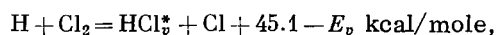
Thus in this case the chain reaction mechanism is provided by oxygen atoms in an electronically excited state and by O_2 molecules with excess energy. According to Norrish^[26] these molecules are vibrationally excited, and according to Semenov^[27] they are electronically excited molecules in the state $^3\Sigma_u^-$ (excitation energy 142.4 kcal/mole) appearing in the interaction of $\text{O}(^1\text{D})$ atoms with O_3 molecules.

As has already been indicated at the beginning of this section, Bodenstein attempted as far back as 1916 to explain the chain mechanism of the reaction of chlorine with hydrogen on an energy basis. In 1934 Semenov^[4] showed with the aid of a mechanism analogous to that of Bodenstein that in a reaction which under usual conditions occurs in straight (unbranched) chains there is in principle a possibility of branching. Semenov's idea consisted in the fact that the energy-rich HCl molecules (HCl^*) appearing in the process



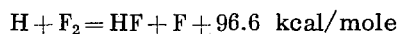
can in colliding with a chlorine molecule having sufficient energy dissociate it into atoms (the heat of dissociation of Cl_2 is 57.1 kcal/mole). As a result there appear two additional chains (branching).

Recently Semenov^[27] undertook to justify quantitatively the possibility of the energy branching proposed by him in the reaction of chlorine with hydrogen and concluded that in the present state of our knowledge about the dynamics of the elementary chemical process and energy exchange processes in the collisions of molecules this problem cannot be solved. Measurements^[28] of the relative values of the rate constants of the process



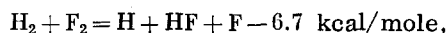
where HCl^* is a vibrationally excited HCl molecule in a state v and E_v is its vibrational energy, showed that an overwhelming number of the HCl molecules appears in the zeroth vibrational state ($E_v = 0$) and only 0.015% of the newly formed HCl molecules are on the $v = 6$ level which corresponds to an energy of 45.5 kcal/mole. The small fraction of the molecules which possess a large amount of vibrational energy at the time of their formation in the interaction of H with Cl_2 , together with the large probability of the diffusion of the translational and rotational energies in molecular collisions, make it improbable that the branching proposed by Semenov plays an important role in the reaction of chlorine with hydrogen.

Another matter is the analogous reaction of fluorine with hydrogen where the thermal effect of the process

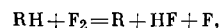


exceeds the heat of dissociation of a fluorine molecule by a factor of 2.5. One can therefore assume that in this case the number of HF^* molecules with an energy sufficient for dissociation of F_2 will be considerably larger than the number of HCl molecules. Consequently one should expect that the energy mechanism of the branching of the reaction of fluorine with hydrogen will be probable.^[27] One can consider one manifestation of this to be the ease with which fluorine-hydrogen mixtures explode, even at low temperatures.^[29]

The ease with which fluorine reacts with hydrogen (and also with hydrocarbons) is undoubtedly connected with the small activation energy of the initiation of chains according to the scheme^[30]

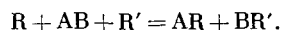


*An analogous scheme for the reaction of F_2 with the hydrocarbons of the paraffin series



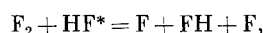
was apparently first postulated by Miller and his co-workers^[31] who provided weighty proof of its correctness on the basis of an analysis of the reaction products.

Starting from the idea that a reaction of a radical with a molecule occurs as a rule much more readily than a reaction between two saturated molecules, the reaction of a saturated molecule with two radicals should occur even more readily



Semenov postulated^[30] the inverse process to be one of the main processes of the formation of free radicals in the interaction of saturated molecules. A large binding energy of the molecule AB is a condition for the ready occurrence of this process. According to Semenov, in the case of endothermic processes the activation energy of this process should be close to its thermal effect, whereas in the case of exothermic processes it should be close to zero.^[31] Numerous examples confirming Semenov's ideas are cited in Semenov's book^[30] and in the subsequent literature*.

The H and F atoms produced in the interaction of fluorine with hydrogen according to the above scheme interact respectively with the fluorine and hydrogen molecules and give rise to an unbranched chain reaction (Nernst chain). However, the energy-rich HF* molecules resulting from the interaction of H with F₂ also turn out to be capable of splitting fluorine molecules:



which serves as an additional source of free radicals and initiates two new chains. Thus the reaction becomes branched, which leads to an explosion †.

The branched nature of the reaction of fluorine with hydrogen follows quite obviously from the first and second inflammability limits of fluorine-hydrogen mixtures recently discovered in the experiments of A. E. Shilov and his co-workers.^[33] The first limit was established by observing the flare-up of a fluorine-hydrogen mixture entering an evacuated vessel: the flare-up occurred only after the pressure of the mixture reached a certain limiting minimum value p_1 . The second limit was determined by two methods: one consisted in observing the flare-up of a fluorine-hydrogen mixture taking place when the pressure of the mixture dropped to a certain limiting value p_2 ; the other method

consisted in observing the flare-up of a mixture prepared at liquid nitrogen temperature and rapidly heated to a certain temperature; the flare-up occurred only when the pressure of the mixture was less than p_2 . The second inflammability limit of a (F₂):(H₂) = 0.09 mixture measured by the latter method at various temperatures is shown in Fig. 4.

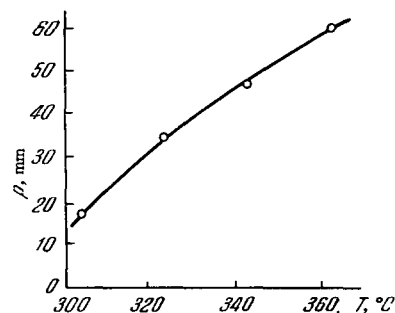
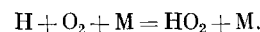
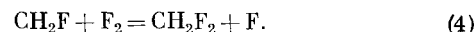
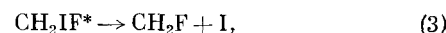
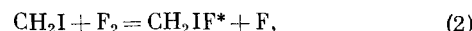
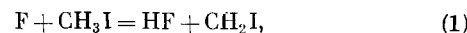


FIG. 4. The second inflammability limit of a mixture of hydrogen and fluorine.^[33]

In order to explain the inflammability limits, one must supplement the above reaction mechanism of fluorine with hydrogen with chain breaking processes. It is natural to relate the lower inflammability limit to the breaking of chains at the walls; as regards the upper limit, it was shown in^[33] that all the observed regularities can be explained if the volume breaking of chains is ascribed to the effect of oxygen (small quantities of which are present in the mixture) taken up by the hydrogen in the process

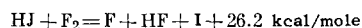


Whereas the chain branching in the reaction of fluorine with hydrogen is the result of intermolecular energy exchange ($HF^* + F_2 = HF + 2F$), in the reaction of fluorine with CH₃I branching occurs, as was shown by Shilov and co-workers,^[34] as a result of intramolecular energy exchange. The mechanism of this reaction is:



Branching occurs here as a result of the fact that the energy (about 80 kcal/mole) released in process (2) exceeds by 25 kcal/mole the energy of the C—I bond in the CH₂IF* molecule (about 55 kcal/mole). If the portion of the released energy contained in the CH₂IF* molecule exceeds 55 kcal/mole and the molecule has no time to stabilize, then it will split according to scheme (3) as a result of an internal energy redistribution. By supplying an additional amount of fluorine atoms which lead the chain reaction, process (4) gives rise to branching of the chains.

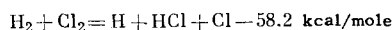
*Shilov and his co-workers^[32] observed for the process



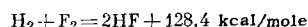
the rate constant

$$k = 3 \cdot 10^{10} e^{-3500/RT} \text{ cm}^3 \text{ mole}^{-1} \text{ sec}^{-1}.$$

We note that unlike the reaction of fluorine with hydrogen, the analogous reaction of chlorine with hydrogen is strongly endothermic.



†In view of the large heat of the reaction



one must assume that the initial chain explosion goes over rapidly into a thermal one.

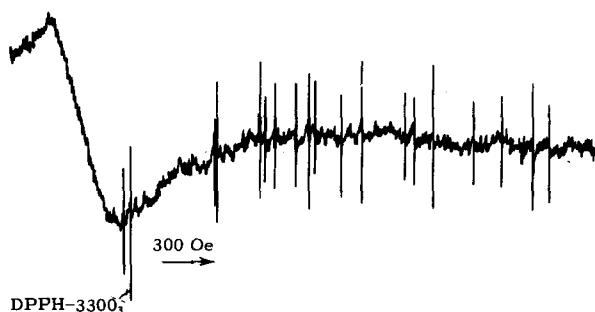


FIG. 5. EPR spectrum of iodine atoms in a $\text{CH}_3\text{I} + \text{F}_2$ flame. The pressure in the vessel was 0.9 mm Hg, $p_{\text{CH}_3}/p_{\text{F}_2} = 1.1$, the temperature $\sim 100^\circ\text{C}$, and the concentration of iodine atoms $\sim 10^{14}$ atom/cm³.

In accordance with the reaction mechanism in [34], molecular iodine was observed in the reaction products, iodine atoms in the EPR spectrum (Fig. 5), and IF bands in the spectrum of the flame; this is evidence of the presence of iodine and fluorine atoms in the reaction zone.

The reactions of fluorine with hydrogen and methyl iodide are undoubtedly not the only examples of radical-energy branched chain reactions of fluorine. N. N. Semenov presented in his paper before the Royal Society (in 1965) the following table:

RH	$\Delta E = Q - D$, kcal/mole	RH	$\Delta E = Q - D$, kcal/mole
H_2	-37	CH_3Br	+10
CH_4	-21	CH_3NO_2	+19
CH_3OH	-13	CH_3I	+24
CH_3Cl	-3	CH_3ONO_2	+39
CH_3SH	+7	CH_3ONO	+41

The RH molecules with which the fluorine atoms interact according to the scheme $\text{F} + \text{RH} = \text{R} + \text{HF}$ are shown in the first column of the table; the second column lists the values of $\Delta E = Q - D$ where Q is the heat of the reaction $\text{R} + \text{F}_2 = \text{R} + \text{F}$ and D is the energy of dissociation of the RF molecule into two new radicals ($\text{RF} = \text{R}^{\text{I}} + \text{R}^{\text{II}}$). Semenov indicates that in radical-energy chain reactions of fluorine with substances for which $\Delta E < 0$ branching is possible by means of intermolecular energy exchange, whereas in reactions when $\Delta E > 0$ it is possible by means of intramolecular energy exchange.

Thus the number of branched chain reactions turns out to be considerably larger than has hitherto been assumed. It should also be noted that the energy factor in branched chain reactions has been underestimated so far. The importance of this factor is particularly great in chemical reactions taking place at high temperatures.

¹ M. Bodenstein, Z. physik. Chem. **85**, 329 (1913).

² J. Stark, Physik. Z. **9**, 889 (1908); Prinzipien der

Atomdynamik, v. 2, Hirzel, Leipzig, 1911, p. 207; Ann. Phys. **38**, 467 (1912); A. Einstein, Ann. Physik. **37**, 832 (1912); Ann. Phys. **38**, 881 (1912); J. Physik. **3**, 277 (1913).

³ W. Nernst, Z. Elektrochem. **24**, 335 (1918).

⁴ N. N. Semenov, Tsepnye reaktsii (Chain Reactions), Leningrad, 1934.

⁵ N. N. Semenov, Z. Physik. Chem. **B2**, 161 (1929).

⁶ C. R. Patrick and J. C. Robb, Trans. Farad. Soc. **51**, 1697 (1955).

⁷ V. V. Voevodskii, Zh. fiz. khim. **20**, 1285 (1946); A. H. Wilbourn and C. N. Hinshelwood, Proc. Roy. Soc. **A185**, 353 (1946).

⁸ A. B. Nalbandyan and V. V. Voevodskii, Mekhanizm okisleniya i gorennya vodoroda (Oxidation and Combustion Mechanism of Hydrogen), M.-L., AN SSSR, 1949, Sec. 24.

⁹ A. G. Gaydon and H. G. Wolfhard, Proc. Roy. Soc. **A199**, 89 (1949).

¹⁰ A. G. Gaydon and H. G. Wolfhard, Flames, London, 1953, p. 247.

¹¹ V. Kondrat'ev and M. Ziskin, Zh. fiz. khim. **10**, 360 (1937).

¹² F. J. Lipscomb, R. G. Norrish, and B. A. Thrush, Proc. Roy. Soc. **A233**, 455 (1955).

¹³ D. R. Bates and M. Nicolet, Publ. Astr. Soc. Pac. **62**, 106 (1950); Compt. rend. **230**, 1943 (1950); J. Geograph. Res. **55**, 301 (1950); G. Herzberg, J. Roy. Astr. Soc. Canada **45**, 100 (1951).

¹⁴ A. B. Meinel, Astr. J. **111**, 555 (1950); **112**, 120 (1950).

¹⁵ J. D. McKinley, D. Garvin, and M. J. Boudart, J. Chem. Phys. **23**, 784 (1955).

¹⁶ D. Garvin, H. P. Broida, and H. J. Kostkowski, J. Chem. Phys. **32**, 880 (1960).

¹⁷ V. F. Shuvalov, R. F. Vasil'ev, L. M. Postnikov, and V. Ya. Shlyapintokh, DAN SSSR **148**, 388 (1963); L. M. Postnikov and V. Ya. Shlyapintokh, DAN SSSR **150**, 340 (1963).

¹⁸ E. Kondrat'eva and V. Kondrat'ev, Zh. fiz. khim. **9**, 746 (1937).

¹⁹ R. D. Schultz and H. A. Taylor, J. Chem. Phys. **18**, 194 (1950).

²⁰ E. W. R. Steacie, Atomic and Free Radical Reactions, N.Y. 1954, p. 743.

²¹ M. Bodenstein, Z. Elektrochem. **22**, 53 (1916).

²² J. A. Christiansen and H. A. Kramers, Z. Physik. Chem. **104**, 451 (1923).

²³ K. E. Shuler, Fifth Symposium on Combustion, N.Y., 1955, p. 56.

²⁴ L. J. Heidt and G. S. Forbes, J. Am. Chem. Soc. **56**, 2365 (1934); L. J. Heidt, J. Am. Chem. Soc. **57**, 1710 (1935).

²⁵ G. B. Kistiakowsky, Z. Physik. Chem. **117**, 337 (1925).

²⁶ R. G. W. Norrish, in coll. Trasfert d'energie dans les gas, 12-me Conseil de Chimie (Solvay), 1962, p. 99.

²⁷ N. N. Semenov, *ibid.* p. 183.

- ²⁸J. R. Airay, R. R. Getty, J. C. Polanyi, and D. R. Snelling, *J. Chem. Phys.* **41**, 3255 (1964).
- ²⁹A. V. Grosse and A. D. Kirschenbaum, *J. Am. Chem. Soc.* **77**, 512 (1955).
- ³⁰N. N. Semenov, *O nekotorykh problemakh khimicheskoi kinetiki i reaktsionnoi sposobnosti (Concerning Certain Problems of Chemical Kinetics and Reactivity)*, Ch. 3, Secs. 8 and 9, M., 1958.
- ³¹W. T. Miller, S. D. Koch, and F. W. McLafferty, *J. Am. Chem. Soc.* **78**, 4992 (1956); W. T. Miller and D. Koch, *J. Am. Chem. Soc.* **79**, 3084 (1957).
- ³²G. A. Kapralova, L. Yu. Rusin, A. M. Chaikin, and A. E. Shilov, *DAN SSSR* **150**, 1282 (1963).
- ³³G. A. Kapralova, E. L. Trofimova, and A. E. Shilov, *Kinetika i kataliz* **6**, 977 (1965).
- ³⁴G. A. Kapralova, E. A. Trofimova, L. Yu. Rusin, A. M. Chaikin, and A. E. Shilov, *Kinetika i kataliz* **4**, 653 (1963); L. Yu. Rusin, A. M. Chaikin, and A. E. Shilov, *ibid.* **5**, 1121 (1964).
- ³⁵C. N. Hinshelwood and H. W. Thomson, *Proc. Roy. Soc.* **A122**, 610 (1929).
- ³⁶D. Kopp, A. Koval'skiĭ, A. Zagulin, and N. Semenov, *Z. Phys. Chem.* **B6**, 307 (1930); *Zh. fiz. khim.* **1**, 263 (1940).
- ³⁷A. Zagulin, *Z. Phys. Chem.* **B1**, 275 (1928).
- ³⁸W. E. Garner and A. S. Gomm, *Trans. Farad. Soc.* **24**, 470 (1928).
- ³⁹H. B. Dixon, *J. Chem. Soc.* **97**, 661 (1910).

Translated by Z. Barnea