CHEMICAL ACTIVATION

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1. Introduction

Nature of Chemical Activation.—A species which is energised by other than thermal collisional processes displays behaviour characteristic of an energy distribution which is non-equilibrium, relative to the condition of statistical equilibrium for that species at the ambient temperature. If the species is activated in the course of its production by chemical reaction, this process will be called "chemical activation". The further reaction of such species and their energy degradation, whether by radiation or collisional deactivation, can provide information relevant to energy-transfer processes and reaction-rate theory. The actual fate of the excited molecules depends on the relative rates of all possible processes that may ensue; these are a function of the nature and energy content of the molecules. The ability to provide different known energy distributions of excited species represents one advantage of the chemical activation technique. An important aspect is the opportunity presented for study, as in the case of exchange reactions, of the activation reaction itself and of the energy distribution between products.

Limitations of this Review.—This Review brings together known examples of chemical activation systems, which have been accumulating increasingly in recent years, in order to clarify their nature and to exemplify their usefulness. The major emphasis is on activated molecules produced in electronic ground states; these are the simplest systems. Brief mention of some reactions involving electronic excitation will be given, however, since these include important examples of chemical activation.

Some systems, such as atom recombination, have been studied in great detail in recent years[1] and cannot be considered here at length. Ion–molecule activation reactions are arbitrarily omitted; aspects of these have been reviewed recently.[2]

Many chemical activation systems are not amenable to useful discussion, either because of their complexity or because insufficient data are available. Only some of these need be mentioned. This Review is not concerned with experimental techniques, but rather with the information that has been or may be obtained by the use of chemical activation. For the sake of brevity, much of the exposition is given in terms of a restricted number of illustrative examples.

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[1] See Symposium on Inelastic Collisions of Atoms and Small Molecules, *Discuss. Faraday Soc.*, 1962, **33**, for several recent studies and references.

[2] F. W. Lampe, J. L. Franklin, and F. H. Field, "Progress in Reaction Kinetics," ed. G. Porter, Vol. 1, Pergamon Press, London, 1961, p. 67.

2. General Characterisation of Chemical Activation

A. Energy Characteristics of Activation Reactions.—*Microscopic reversibility.* Chemically activated species are energised, either with respect to further reaction or to deactivation. As governed by the principle of microscopic reversibility, the products of reaction are activated for the reverse reaction, if for no other. Thus it would appear that every reaction results in chemical activation. However, in some case, such as exchange and decomposition reactions, the products have energy of relative translation and move apart.[3] In other cases, the reverse reaction cannot be observed; it may occur to such a negligible extent, or so slowly, as to be of no practical concern. Thus, in the elementary isomerisation of methyl isocyanide[4]

$$\mathrm{MeNC} \rightarrow \mathrm{MeCN} + 15\ \mathrm{kcal.}$$

the reverse reaction is not observed. Similarly, for the thermal reaction[5]

$$\text{cyclo-}C_3H_6 \rightarrow CH_3{\cdot}CH{:}CH_2 + 7{\cdot}5\ \mathrm{kcal.}$$

the reverse isomerisation of *ground* electronic state singlet propene is not definitely known.[6]

Exothermic processes. Activation may result from exothermic reaction, whereby energy of reaction appears as internal energy of the products. An instance is the "atom cracking" process[7,8]

$$H + {\cdot}C_2H_5 \rightarrow C_2H_6^* + 98\ \mathrm{kcal.}$$
$$C_2H_6^* \rightarrow 2{\cdot}CH_3$$

where an asterisk* will always signify vibrational excitation. Another example is[9]

$$\mathrm{Cl} + \mathrm{Na}_2 \rightarrow \mathrm{NaCl}^* + \mathrm{Na} + 70\ \mathrm{kcal.}$$

followed by

$$\mathrm{NaCl}^* + \mathrm{Na}(^2S) \rightarrow \mathrm{NaCl} + \mathrm{Na}^\dagger\ (^2P)$$

Here, collisional deexcitation of sodium chloride is manifested by fluorescence of the resulting electronically excited Na†(^2P) atoms. (A dagger† will always signify electronic excitation.)

Some highly exothermic overall reactions do not result in significant

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[3] J. C. Polanyi, *J. Chem. Phys.*, 1959, **31**, 1338.

[4] F. W. Schneider and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, 1962, **84**, 4215.

[5] T. S. Chambers and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1934, **56**, 399; H. O. Pritchard, R. G. Sowden, and A. F. Trotman-Dickenson, *Proc. Roy. Soc.*, 1953, **217**, *A*, 563.

[6] D. W. Setser, B. S. Rabinovitch, and D. W. Placzek, *J. Amer. Chem. Soc.*, 1963, **85**, 862.

[7] (*a*) E. W. R. Steacie, "Atomic and Free Radical Reactions," 2nd edn., Reinhold Publishing Co., New York, 1954; (*b*) N. A. D. Parlee and E. W. R. Steacie, *Canad. J. Res.*, 1939, *B*, **17**, 371.

[8] C. A. Heller and A. S. Gordon, *J. Chem. Phys.*, 1962, **36**, 2648.

[9] (*a*) M. Polanyi, "Atomic Reactions", Williams and Northgate Ltd., London, 1932; (*b*) M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, 1939, **35**, 178.

instances of chemical activation: the nature of the products, or their energy distribution, is such that only inconspicuous collisional deactivation occurs. An example is the decomposition of di-t-butyl peroxide[10]

$$\mathrm{Me_3C{\cdot}O{\cdot}O{\cdot}CMe_3 \rightarrow 2Me_2CO + C_2H_6 + 39\ kcal.}$$

Attention must be focused here on the elementary steps. The production of t-butoxy-radicals

$$\mathrm{Me_3C{\cdot}O{\cdot}O{\cdot}CMe_3 \rightarrow 2Me_3CO^{\bullet} - 38\ kcal.}$$

is not exothermic; the evidence is that these radicals must be activated by collision before undergoing (endothermic[11]) decomposition

$$\mathrm{Me_3CO^{\bullet} \rightarrow Me^{\bullet} + Me_2CO - 3\ kcal.};\ E_a = 15\ \mathrm{kcal.\ mole^{-1}}$$

The overall exothermicity results from recombination of methyl to give ethane.

The overall decomposition of acetyl peroxide is somewhat similar:

$$\mathrm{(Me{\cdot}CO{\cdot}O{\cdot})_2 \rightarrow C_2H_6 + 2CO_2 + 100\ kcal.}$$

Actually, the exothermicity here does not result exclusively from methyl combination, but also in part from the decomposition of acetoxy-radicals with reorganisation energy[12] of the products:

$$\mathrm{(Me{\cdot}CO{\cdot}O{\cdot})_2 \rightarrow 2\ Me{\cdot}CO{\cdot}O{\cdot} - 37\ kcal.}$$

$$\mathrm{Me{\cdot}CO{\cdot}O{\cdot} \rightarrow Me{\cdot} + CO_2 + 17{\cdot}5\ kcal.}$$

The exothermicity of the second reaction is shared between the products.

Some elementary step in an overall exothermic reaction *must* produce species with excess of energy. But unless the latter exhibit some special reaction property or easily apprehended behaviour, as in the chlorine atom–sodium system, all that occurs is thermal equilibration, possibly observable as an increase in temperature. Special efforts can, however, lead to more useful results in some cases. Thus, in the reaction

$$\mathrm{H + Cl_2 \rightarrow HCl^* + Cl}$$

the hydrogen chloride molecule produced is vibrationally excited and heating occurs; but, in addition, spectroscopic measurement of vibrational emission leads to valuable data.[13]

Endothermic processes. Activated molecules may arise by an endothermic process. The reaction of iodine atoms with 1,2-disubstituted ole-

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[10] J. H. Raley, F. F. Rust, and W. E. Vaughan, *J. Amer. Chem. Soc.*, 1948, **70**, 88; L. Batt and S. W. Benson, *J. Chem. Phys.*, 1962, **36**, 895.

[11] H. Hershenson and S. W. Benson, *J. Chem. Phys.*, 1962, **37**, 1889.

[12] L. Jaffe, E. J. Prosen, and M. Szwarc, *J. Chem. Phys.*, 1957, **27**, 416; cf. also J. E. Lennard-Jones, *Trans. Faraday Soc.*, 1934, **30**, 70; R. E. W. Norrish and L. H. Long, *Proc. Roy Soc.*, 1946, **187**, *A*, 337.

[13] P. E. Charters and J. C. Polanyi, *Discuss. Faraday Soc.*, 1962, **33**, 107.

fins[14,15] to produce iodo-radicals is ~9 kcal. $mole^{-1}$ endothermic. The iodo-radicals necessarily are formed with sufficient energy for the reverse decomposition to occur and the olefin produced may be geometrically isomerised.

Potential energy surfaces. Schematic potential energy diagrams are given in Fig. 1 for some general exothermic schemes, and in Fig. 2 for endothermic processes. A, B, and C each represent one or more species. B will normally include the chemically activated product species.

Fig. 1(*a*) is the case where B undergoes no reaction of interest other than the reverse. Examples are[16]

$$cis\text{-stilbene} \rightarrow trans\text{-stilbene}$$

and[17]

$$2\cdot NF_2 \rightarrow N_2F_4$$

Cases (*b*) and (*c*) illustrate the occurrence of further reactions of B which are exothermic and endothermic, respectively; this distinction is only of formal importance in most cases. Instances of (*b*) and (*c*) respectively, are[18]

$$:CH_2 + cis\text{- but-2-ene} \rightarrow cis\text{-dimethylcyclopropane}^*$$
$$cis\text{-dimethylcyclopropane}^* \rightarrow \text{pentenes}$$

and[19]

$$H + cis\text{-}C_4H_8 \rightarrow \cdot C_4H_9^*$$
$$\cdot C_4H_9^* \rightarrow \cdot CH_3 + C_3H_6$$

In practice, case (*d*) represents the situation where not all excitation levels of B constitute activation for a subsequent reaction to give C, or where only very modest further thermal excitation of B must occur,[20]

$$H + trans\text{-}C_2H_2D_2 \rightarrow \cdot C_2H_3D_2^* + 38 \text{ kcal.}$$
$$\cdot C_2H_3D_2^* \rightarrow D + C_2H_3D - 40 \text{ kcal.}$$

A larger threshold energy for production of C would transform case (*d*) into case (*a*).

Evidently, the microscopic reverse processes of those just described, B → A, correspond to endothermic chemical activation; Fig. 2(*a*) is simply the reflection of Fig. 1(*a*). The distinction between the two cases is not trivial, however, since reactions were described at the outset of Section 2 where only one of the "reversible" processes can be studied

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[14] H. Steinmetz and R. M. Noyes, *J. Amer. Chem. Soc.*, 1952, **74**, 4141.

[15] M. H. Back and R. J. Cvetanović, *Canad. J. Chem.*, 1963, **41**, 1396.

[16] G. B. Kistiakowsky and W. R. Smith, *J. Amer. Chem. Soc.*, 1934, **56**, 638; 1936, **58**, 766; M. Calvin and H. W. Alter, *J. Chem. Phys.*, 1951, **19**, 768; A. Dyck and D. M. McLure, *J. Chem. Phys.*, 1962, **36**, 2326.

[17] F. A. Johnson and C. B. Colburn, *J. Amer. Chem. Soc.*, 1961, **83**, 3043.

[18] H. M. Frey, *Proc. Roy. Soc.*, 1959, *A*, **251**, 575.

[19] B. S. Rabinovitch and R. W. Diesen, *J. Chem. Phys.*, 1959, **30**, 735.

[20] B. S. Rabinovitch, D. H. Dills, W. H. McLain, and J. H. Current, *J. Chem. Phys.*, 1960, **32**, 493.

directly. Fig. 2(a') further illustrates such a case, represented by the system[21]

$$trans\text{-}C_2H_2D_2 + NO \rightarrow DH\dot{C}\text{-}C(NO)HD^*$$

The reverse process leads to isomerisation of the olefin. The stability of the nitrosoethyl radical is not known, but quite probably the potential well at B is very shallow. This system cannot be studied in reverse, with B as initial reactant, since the radical cannot be isolated. Although in most systems the activated species B can suffer collisional deactivation, the last system represents an instance where, at the ambient temperature, the average thermal energy of the species may exceed the depth of the potential-energy well characterising B. The excited species *cannot* be collisionally stabilised but may only relax into over-all chemical equilibrium with reactants.

The formation of trimethylene from cyclopropane[22]

$$cyclo\text{-}C_3H_6 \rightarrow \dot{C}H_2\cdot CH_2\cdot \dot{C}H$$

may represent a case intermediate between the surfaces 2(a') and 2(b). At sufficiently high temperature the average thermal energy of trimethylene may exceed the depth of the well;[22,23] investigation of the reverse reaction with trimethylene as initial reactant has been reported,[24] although further work seems necessary.

Further description of systems corresponding to the behaviour represented by these surfaces will be presented in connection with the characterisation of the chemical activation reaction in terms of its molecularity.

B. Reaction Types Giving Rise to Chemical Activation.—Table 1 lists the types of activation reactions to be described. Such consideration allows more precise description of the energy distribution of the activated species.

TABLE 1.

	Reactants, A	*Products*, B	*Reaction type*
(i)	single molecule	single molecule	unimolecular isomerisation
(ii)	single molecule	two or more species	unimolecular decomposition
(iii)	two species	single molecule	bimolecular association
(iv)	two species	two species	bimolecular exchange or displacement
(v)	three species	two species	"trimolecular" reaction

Type (i). *Activation by unimolecular isomerisation.* A product molecule B formed by unimolecular isomerisation automatically has a minimum energy $E_{\min}$ equal to $E_1 \pm \Delta H_1$ (Figs. 1a and 2a). The energy distribution

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[21] B. S. Rabinovitch and F. S. Looney, *J. Chem. Phys.*, 1955, **23**, 2439.

[22] E. W. Schlag and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, 1960, **82**, 5996.

[23] F. H. Seubold, *J. Chem. Phys.*, 1953, **21**, 1616; 1954, **22**, 945; E. W. Schlag, Thesis, University of Washington, 1958.

[24] F. E. Blacet and A. Miller, *J. Amer. Chem. Soc.*, 1957, **79**, 4327; M. C. Flowers and H. M. Frey, *J.*, 1960, 2758.

function above $E_{\min}$ of species B *as formed*, $f(E)$, depends on that of the *reacting* molecules; the latter is given[25] at high pressure ($p \to \infty$) by the Boltzmann distribution $K(E)$ weighted by the specific reaction probability $k(E)$,

$$[f(E)\,\mathrm{d}E]_\infty = k(E)\,K(E)\,\mathrm{d}E;\ E \geqslant E_1 \tag{1}$$

For reaction of A at low pressure ($p \to 0$) the reaction co-ordinate is the collision co-ordinate and

$$[f(E)\,\mathrm{d}E]_0 = K(E)\,\mathrm{d}E;\ E \geqslant E_1 \tag{2}$$

At intermediate pressures,

$$[f(E)\,\mathrm{d}E]_{0<p<\infty} = \frac{k(E)}{k(E)+\omega}\cdot K(E)\,\mathrm{d}E \tag{3}$$

where ω is the specific collision rate.

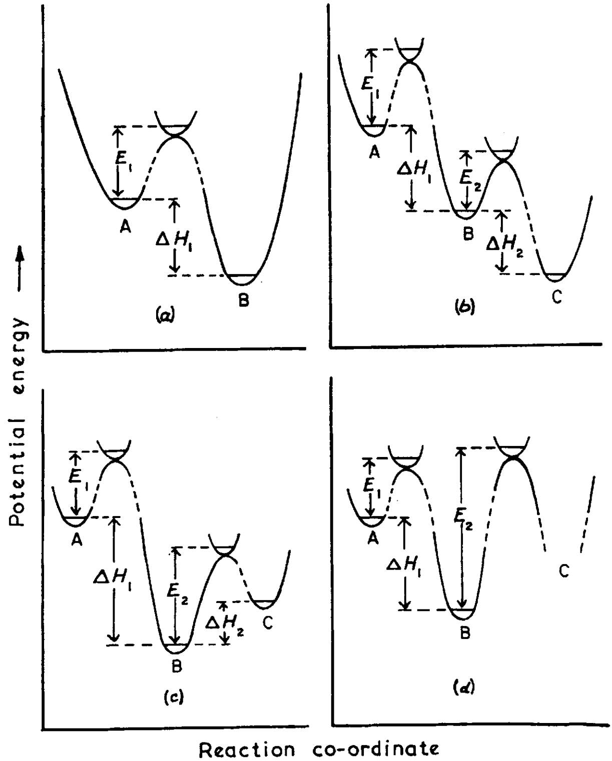

FIG. 1. *Potential-energy curves for exothermic reactions.*

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[25] R. C. Tolman, "Statistical Mechanics," Chemical Catalogue Company, New York, 1927.

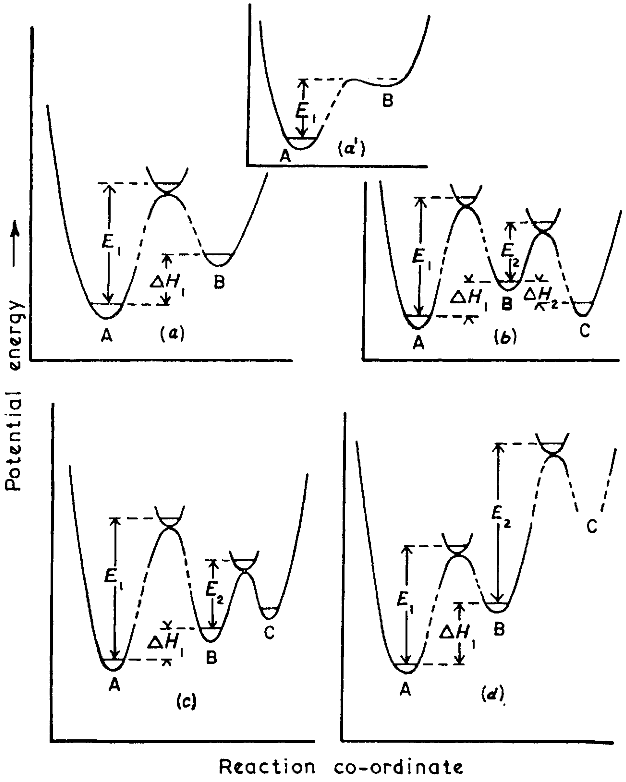
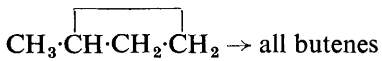


FIG. 2. *Potential-energy curves for endothermic reactions.*

Fig. 1(*a*) represents the case where B may only revert to A if not collisionally deactivated. The isomerisation of olefins[16,26] and azo-compounds[27] are examples of such behaviour. At sufficiently high pressures only collisional deactivation is significant, and subsequent reaction of B, if any, is merely by thermal activation. Illustrations of other type (i) systems are provided in principle by the low-pressure isomerisations of [$^2H_2$]cyclopropane,[22] methylcyclopropane,[28] and of dimethylcyclopropane.[29] Methylcyclopropane, in all of its possible combinations of consecutive reactions,



$CH_3{\cdot}CH{\cdot}CH_2{\cdot}CH_2 \rightarrow$ all butenes

cis-but-2-ene → *trans*-but-2-ene, etc.

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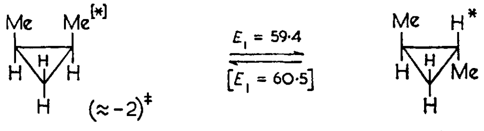
[26] J. E. Douglas, B. S. Rabinovitch, and F. S. Looney, *J. Chem. Phys.*, 1955, **23**, 315; B. S. Rabinovitch and K. W. Michel, *J. Amer. Chem. Soc.*, 1959, **87**, 5065; R. B. Cundall and T. F. Palmer, *Trans. Faraday Soc.*, 1961, **57**, 1936, 2226.

[27] G. S. Hartley, *J.*, 1938, 638; E. Fischer and Y. Frei, *J. Chem. Phys.*, 1957, **27**, 328.

[28] J. P. Chesick, *J. Amer. Chem. Soc.*, 1960, **82**, 3277.

[29] M. C. Flowers and H. M. Frey, *Proc. Roy. Soc.*, 1960, **257**, *A*, 122; 1961, **260**, *A*, 424.

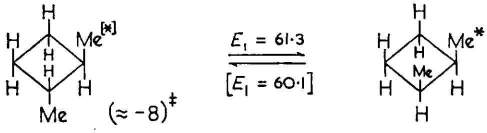
provides examples of all cases of Fig. 1. The dimethyl system provides a number of cases of Fig. 1(*d*) and 2(*d*), depending on whether the initial reactant is the *cis*- or *trans*-isomer. The further reaction of products C to give "D", *e.g.*, *cis*-pentene → *trans*-pentene, might also occur in this instance:



‡The parenthetic quantities are the heats of formation, ΔH_f° kcal. mole^{-1} at 25°. The values for dimethylcyclopropane and dimethylcyclobutane were estimated from comparison of heats of formation of cyclopentane and 1,2-dimethylcyclopentane and of cyclohexane and 1,2-dimethylcyclohexane.

$[E_2]$		E_2
61·4 →	*cis*-$CH_3{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH_3$ (−6·7)	← 63·6
61·2 →	*trans*-$CH_3{\cdot}CH_2{\cdot}CH{=}CH{\cdot}CH_3$ (−7·6)	← 62·9
62·3 →	$(CH_3)_2C{=}CH{\cdot}CH_3$(−10·2)	← 62·3
61·9 →	$CH_3{\cdot}CH_2{\cdot}C(CH_3){=}CH_2$(−8·7)	← 61·9

A related system is the geometrical isomerisation and decomposition of *trans*-1,2-dimethylcyclobutane.[30] Here the activation energies for geometrical isomerisation (61·3 kcal.) and for the two modes of decomposition (~60·4 and 63·0 kcal.) are very similar; these represent Figs. 2(*b*) and 2(*d*).



$[E_2]$		E_2
61·6 →	$2C_3H_6$ (10)	← 60·4
63·4 →	C_2H_4 + *cis*- and *trans*-C_4H_8 (10)	← 63·0

cis-1,2-Dimethylcyclobutane as initial reactant provides another example of 1(*d*). The present type of activation reaction allows the interesting possibility, at low pressures, of molecules B reacting at a rate characterised by the energy-distribution function of A.

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[30] H. R. Gerberich and W. D. Walters, *J. Amer. Chem. Soc.*, 1961, **83**, 3935, 4884.

Type (ii). Activation by unimolecular decomposition. The products of reaction of type (ii) have $E_{\mathrm{min}} = E_1 \pm \Delta H_1$, and a *total* energy-distribution function which is the same as for type (i). For most chemical reactions it is not possible to predict *precisely* how this energy will be divided. Part, at least, must go into relative translational energy of the products. If B consists of two (electronically unexcited) atoms, the energy is converted into relative translational energy and is divided between the two products in an inverse function of their masses, as governed by momentum conservation.

For two molecular products, a qualitative picture of the internal energy distribution can be obtained in some cases. If a bond (or bonds) in one product becomes significantly shortened relative to its length in the transition state, such products will tend to contain excess of vibrational energy. In the thermal decomposition of diazomethane

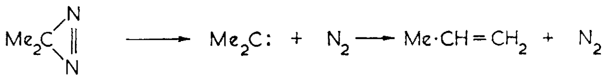
$$CH_2N_2 \rightarrow :CH_2 + N_2^*$$

the N–N distance shortens from 1·13 Å to 1·095 Å;[31] the nitrogen molecule would be expected to be vibrationally excited. This seems to be the case, although the singlet methylene product also carries some of the excess energy.[32]

Further examples include the decomposition of hydrogen azide in the presence of recombining hydrogen atoms.[33] The decomposition is stated to produce NH radicals in both singlet and triplet states which give rise to emission:

$$N_3H(\text{triplet}) + M \rightarrow N_2(^1\Sigma) + NH(^3\Pi) + M$$
$$NH(^3\Pi) \rightarrow NH(^3\Sigma) + h\nu$$

The thermal decomposition of dimethyldiazirine[34] forms isopropylidene with sufficient energy to rearrange to propene



When E_2 is much larger than $(E_1 + \Delta H_1)$, such that the collisional transition probability $P_{(E_1+\Delta H_1)\rightarrow E_2} \approx 0$, then only deactivation of the products can occur, and subsequent reaction other than the reverse is entirely by thermal activation. This is the case for most decomposition reactions, which give rise to "stable" products.

In general, unimolecular activation reactions are not important categories relative to bimolecular reactions.

Type (iii). Bimolecular association.—The energy of a bimolecular associa-

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[31] Tables of Interatomic Distances and Configuration in Molecules and Ions, Chemical Society Special Publication No. 11, 1958.

[32] D. W. Setser and B. S. Rabinovitch, *Canad. J. Chem.*, 1962, **40**, 1425.

[33] H. Guenebaut and M. Latour, *J. Chim. phys.*, 1962, **59**, 970.

[34] H. M. Frey and I. D. R. Stevens, *J.*, 1962, 3865.

tion process ($E_1 \pm \Delta H_1 +$ thermal energy of reactants), is confined entirely to the product molecule. If E_1, ΔH_1, and the heat capacity of the reactants are known, the energy content of the excited intermediate is also known. The spread of energies depends on the thermal spread of the reactants. The distribution function is given by eqn. (1), assuming thermal equilibrium of the reactants;[19] failure of the latter condition scarcely occurs in practice, even for association reactions of radicals which occur on virtually every collision.[35] The product molecules will, if not deactivated, decompose again into the original reactants [Fig. 1(*a*)] or, if there is an alternative reaction path [Fig. 1(*b*) or 1(*c*)], into other products.

The relaxation time for decomposition of an activated molecule depends on the number and type of its active degrees of freedom, on its vibrational frequency pattern, on its energy content, and on the free energy of activation for decomposition.[36] As examples, consider the associations

$$\begin{array}{rl}
\mathrm{O}(^3P) + \mathrm{O_2} \rightleftharpoons \mathrm{O_3}^* & + \ \ 24\ \text{kcal.}^{37} \\
2{\cdot}\mathrm{C_2H_5} \rightarrow \text{n-}\mathrm{C_4H_{10}}^* & + \ \ 81\ \text{kcal.}^{38} \\
\text{n-}\dot{\mathrm{C}}_3\mathrm{H_7} + {\cdot}\mathrm{CH_3} \rightarrow \text{n-}\mathrm{C_4H_{10}}^* & + \ \ 82\ \text{kcal.}^{39} \\
\mathrm{C_3H_8} + :\mathrm{CH_2} \rightarrow \text{n-}\mathrm{C_4H_{10}}^* & + \sim 89\ \text{kcal.}^{40} \\
\text{n-}\dot{\mathrm{C}}_4\mathrm{H_9} + \mathrm{H} \rightarrow \text{n-}\mathrm{C_4H_{10}}^* & + \ \ 97\ \text{kcal.}^{7a}
\end{array}$$

Each of these vibrationally activated molecules has a different lifetime for decomposition. That of triatomic ozone is the shortest, for a number of reasons including its low number of active degrees of freedom; that of the n-butane, formed with lowest energy by ethyl recombination, is longest. The extremely useful possibility of producing a molecule at different known average energy levels should be noted.

A great variety of reactions under this general heading has been investigated in addition to the above. Examples of each type of system shown in Fig. 1 are known, *e.g.*,

$$\begin{array}{rl}
\mathrm{NH_3} + \mathrm{BF_3} \rightleftharpoons \mathrm{NH_3{\cdot}BF_3}^* & + 28\ \text{kcal.}^{41}\ [\text{Fig. } 1(a)] \\
\mathrm{R}{\cdot} + \mathrm{NO_2} \rightleftharpoons \mathrm{R{\cdot}O{\cdot}NO}^* & + 57\ \text{kcal.}^{42} \\
\mathrm{R{\cdot}O{\cdot}NO}^* \rightleftharpoons \mathrm{RO}{\cdot} + \mathrm{NO} & - 37\ \text{kcal. } [\text{Fig. } 1(c)]
\end{array}$$

The $\mathrm{C_4H_{10}}^*$ systems above correspond to Fig. 1(*c*). The reactions of methylene radicals and hydrogen atoms with olefins cited in Sect. 2*A* are relevant here also as examples of Fig. 1(*b*), 1(*c*), and 1(*d*). These systems are discussed later in more detail.

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[35] R. D. Present, *J. Chem. Phys.*, 1959, **31**, 747; B. H. Mahan, *ibid.*, 1960, **32**, 362.

[36] R. A. Marcus, *J. Chem. Phys.*, 1952, **20**, 359.

[37] (*a*) F. Kaufmann, *Proc. Roy. Soc.*, 1958, **247**, *A*, 123; (*b*) L. Elias, E. A. Ogryzlo, and H. I. Schiff, *Canad. J. Chem.*, 1959, **37**, 1680.

[38] A. Shepp and K. O. Kutschke, *J. Chem. Phys.*, 1957, **26**, 1020.

[39] P. Ausloos and E. W. R. Steacie, *Canad. J. Chem.*, 1955, **33**, 1062; C. A. Heller, *J. Chem. Phys.*, 1958, **28**, 1255.

[40] J. A. Bell and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1962, **84**, 3417.

[41] F. T. Smith, and G. B. Kistiakowsky, *J. Chem. Phys.*, 1959, **31**, 621.

[42] P. Gray, *Trans. Faraday Soc.*, 1955, **51**, 1367.

Type (*iv*), *Bimolecular exchange.* In this type, the processes of interest have been principally radiative emission or collisional deactivation to the ground state of one or both of the products [Fig. 1(*a*)]. These have been studied mainly by the observation of emission (or absorption) spectra in flash photolysis[43] or diffusion-emitter flame[3] systems. In a few alleged cases[44,45] the ability of one of the products to initiate the decomposition of another species [Fig. 1(*b*) or 1(*c*)] has been described.

An interesting example is provided by ozone. In the thermal decomposition of ozone,[46a] $O_3 \rightarrow O_2 + O(^3P)$, the exchange reaction $O(^3P) + O_3 \rightarrow O_2^* + O_2$ occurs; one molecule carries most of the vibrational excitation in the latter bimolecular reaction,[46] which is the chemical activation step of interest. Although further decomposition of O_3 by energy chains involving vibrationally excited O_2^* ($v > 19$) occurs in the photolytic (blue light) decomposition of ozone[46b,c] [in which $O(^1D)$ atoms are produced], the evidence is against their effective participation in the thermal decomposition. In the latter system, the chemically activated O_2^* molecules suffer collisional deactivation as their principal fate.

It would be expected that very many exothermic reactions would exhibit non-equilibrium infrared emission (Table *B*, Appendix). However, unless the emission is intense, information on the initial energy states of the products is difficult to obtain. Even in favourable cases the interpretations have not been unambiguous.[13] The energy of reaction may be distributed in various ways. For a simple three-centre exchange reaction, $P + QR \rightarrow PQ + R$, Polanyi[3] used a simplified valence-bond argument to demonstrate that in suitable cases almost the entire heat of reaction may appear as vibrational energy of the product PQ. Smith[47] found by a dynamical analysis of a colinear system that the maximum fraction of the energy of reaction retained in the newly formed bond is limited by the kinematic factor $\sin^2 \beta$, where β is the angle of rotation required to take a co-ordinate system describing the reactants into one describing the products, and $\tan^2 \beta = (M_P/M_Q) + (M_Q/M_R) + (M_Q^2/M_PM_R)$; M is the mass of the particle. By taking non-colinearity into account, Bunker[48] concluded that the maximum fraction of the energy of reaction which can appear in the newly-formed bond is larger than that previously predicted. This removed

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[43] N. Basco and R. G. W. Norrish, (*a*) *Canad. J. Chem.*, 1960, **38**, 1769; (*b*) *Proc. Roy. Soc.*, 1961, **260**, *A*, 293.

[44] M. A. A. Clyne and B. A. Thrush, *Trans. Faraday Soc.*, 1961, **57**, 2176; F. P. Del Greco and F. Kaufman, *Discuss. Faraday Soc.*, 1962, **33**, 128.

[45] (*a*) F. Kaufman and J. R. Kelso, *J. Chem. Phys.*, 1958, **28**, 510; (*b*) L. F. Phillips and H. I. Schiff, *ibid.*, 1962, **36**, 1509, 3283; (*c*) J. E. Morgan, L. F. Phillips, and H. I. Schiff, *Discuss. Faraday Soc.*, 1962, **33**, 118; (*d*) J. E. Morgan and H. I. Schiff, *Canad. J. Chem.*, 1963, **41**, 903.

[46] (*a*) S. W. Benson and A. E. Axworthy, jun., *J. Chem. Phys.*, 1957, **26**, 1718; E. Castellano and H. J. Schumacher, *ibid.*, 1962, **36**, 2238; (*b*) W. D. McGrath and R. G. W. Norrish, *Proc. Roy. Soc.*, 1960, **254**, *A*, 317; (*c*) L. F. Phillips and H. I. Schiff, *J. Chem. Phys.*, 1962, **37**, 924.

[47] F. T. Smith, *J. Chem. Phys.*, 1959, **31**, 1352.

[48] D. L. Bunker, *Nature*, 1962, **194**, 1277; N. C. Blais and D. L. Bunker, *J. Chem. Phys.*, 1962, **37**, 2713; 1963, **39**, 315.

some disagreement with experimental results which had previously been interpreted[43] as contravening Smith's model.

Type (*v*). *Trimolecular reactions.* This reaction type is the limiting case of bimolecular associations, which may be described as occurring by three-body collisions;[49] it should be understood that this terminology is simply convenient formalism.

Three types of mechanism have been proposed for atomic association processes[50,51]

$$\begin{array}{ll}
\left.\begin{array}{lll} X & + X \rightleftharpoons X_2^* & \\ X_2^* & + M \rightarrow X_2 + M & \end{array}\right\} & (a) \\
\left.\begin{array}{lll} X & + M \rightleftharpoons XM^* & \\ XM^* & + X \rightarrow X_2 + M & \end{array}\right\} & (b) \\
\left.\begin{array}{lll} X & + M \rightleftharpoons XM^* & \\ XM^* & + M \rightleftharpoons XM + M & \\ XM & + X \rightarrow X_2 + M & \end{array}\right\} & (c)
\end{array}$$

where the excited species B are in this case the complexes X_2^* or XM^*. Both have very short lifetimes if M is atomic and decompose again unless collision with M or X occurs in a time which may be not much longer than the order of the period of molecular vibrations. Common reactions of this type include[1,52]

$$\begin{array}{l}
3I \rightarrow I_2 + I, \\
2I + He \rightarrow I_2 + He, \\
2O + Ar \rightarrow O_2 + Ar
\end{array}$$

If, as in case (*c*), XM is a complex of particular stability,[51] the system is similar to the bimolecular association considered previously.

The energy released on recombination of atoms or small molecules may be very large. A product molecule which is stabilised against decomposition may still have sufficient energy to initiate the decomposition of another substance, as alleged for the induced decomposition of hydrogen azide in the presence of recombining H atoms,[33] or as suggested in the combination of oxygen atoms with carbon monoxide:[53]

$$\begin{array}{l}
O + CO \rightarrow CO_2^* \text{ (singlet)} + 127 \text{ kcal.} \\
CO_2^* + O_2 \rightarrow CO_2 + 2O(^3P)
\end{array}$$

although the details of the combination are not certain.[54] Or it may bring about some other process such as well-known instances[55] of electronic excitation by collisions of the first kind

[49] E. Rabinowitch, *Trans. Faraday Soc.*, 1937, **33**, 283.

[50] G. Porter, *Discuss, Faraday Soc.*, 1961, **33**, 198.

[51] M. I. Christie, *J. Amer. Chem. Soc.*, 1962, **84**, 4066.

[52] (*a*) D. L. Bunker and N. Davidson, *J. Amer. Chem. Soc.*, 1958, **80**, 5085, 5090; (*b*) R. L. Strong, J. C. W. Chien, P. E. Graf, and J. W. Willard, *J. Chem. Phys.*, 1957, **26**, 1287; (*c*) G. Porter and J. A. Smith, *Nature*, 1959, **184**, 446; *Proc. Roy. Soc.*, 1961, **261**, *A*, 28; (*d*) R. R. Reeves, G. Mannella and P. Harteck, *J. Chem. Phys.*, 1960, **32**, 632.

[53] B. H. Mahan and R. B. Solo, *J. Chem. Phys.*, 1962, **37**, 2669.

[54] M. A. A. Clyne and B. A. Thrush, *Proc. Roy. Soc.*, 1962, **269**, *A*, 404.

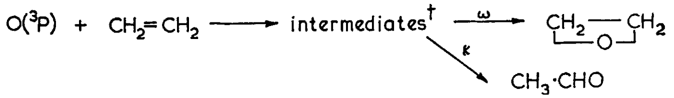
[55] L. F. Phillips and T. M. Sugden, *Trans. Faraday Soc.*, 1961, **57**, 2188.

$$\begin{aligned} 2\,\mathrm{H} + \mathrm{M} &\rightarrow \mathrm{H_2}^* + \mathrm{M} \\ \mathrm{H_2}^* + \mathrm{Pb} &\rightarrow \mathrm{Pb}\dagger + \mathrm{H_2} \\ \mathrm{Pb}\dagger &\rightarrow \mathrm{Pb} + h\nu \end{aligned}$$

Since energy removal by M is a function of the nature of the particles involved, only broad generalisations on the energy level of the association product can be made. In general, for the association of atoms or diatomic molecules in the presence of another atom or diatomic molecule, deactivation of excited product B is to levels only a little below the dissociation limit. If M is a larger species, or one which interacts strongly with the nascent molecule, the immediate deactivation energy level will be significantly lower.

C. Chemical Activation involving Electronic Excitation.—For effective understanding of reactions involving excited electronic states, detailed correlations between the various potential surfaces of the reactants and products are necessary. In most cases adequate information is not available about the topography and topology of the excited surfaces. Difficulties in the interpretation of mechanisms and in the calculation of rates usually arise when complex electronically excited species are involved. Even the ostensibly simple case of recombination of nitrogen atoms in the ground state has provided an extraordinarily complex system involving unstable intermediate molecules.[56]

Ground state reactants which produce electronically excited products. Oxygen atoms in the ground state react with ethylene (olefins in general)[57a] to give acetaldehyde and ethylene oxide, as important primary products,



The reaction is interpreted in terms of the initial formation of an electronically excited triplet intermediate. Collisional deactivation gives rise to ethylene oxide. Uncertainty exists whether in forming the epoxide the spin change occurs before vibrational deactivation, or after, and whether migration of hydrogen occurs in the electronically excited intermediate or in a ground-state intermediate. The relative positions of the various surfaces are not known. This typifies the difficulties encountered in non-adiabatic systems.

An analogous system is that in which $:\mathrm{CH_2}(^3\Sigma_g^-)$ adds to olefins to form the corresponding electronically excited triplet cyclopropane:[58]

If spin angular momentum is not conserved in a reaction, the rate may be considerably reduced.[59] There are instances, however, where the rate of

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[56] G. G. Manella, *Chem. Rev.*, 1963, **63**, 1.

[57] (*a*) R. J. Cvetanović, *J. Chem. Phys.*, 1955, **23**, 1375; 1959, **30**, 19; (*b*) S. Sato and R. J. Cvetanović, *Candad. J. Chem.*, 1958, **36**, 1668.

[58] F. J. Duncan and R. J. Cvetanović, *J. Amer. Chem. Soc.*, 1962, **84**, 3592.

[59] K. J. Laidler and K. E. Shuler, *Chem. Rev.*, 1951, **48**, 153.

$$:CH_2 + R^1HC{=}CHR^2 \longrightarrow R^1HC\text{—}CHR^2\,^{\dagger}$$

such reactions is not governed by the step involving the change of spin, as in the $Hg(^3P_1)$ photosensitised isomerisation of olefins such as but-2-ene,[60] and in the overall reaction of oxygen atoms with carbon monoxide *via* the $CO_2(^3B_2)$ state[53,54]

$$O(^3P) + CO(^1\Sigma^+) \rightarrow CO_2(^1\Sigma_g^+)$$

Electronically excited reactants producing ground-state products. The reactions of the products are usually easier to interpret in this case. We restrict our illustration to a few reactions of the versatile oxygen atom. The $O(^1D)$ state lies 45 kcal. above the triplet ground state. The atoms should react[57b] with ethylene to give a vibrationally-excited, electronic ground state product, since the excess of energy of the reaction, estimated at 129 kcal. mole^{-1}, is considerably less than the vertical difference between the ground state and the first excited singlet state of ethylene oxide (167 kcal. mole^{-1}).[61] Subsequent reactions of the excited ethylene oxide may be treated as ground state adiabatic processes.

$O(^1D)$ also reacts with HCl and H_2O to give vibrationally-excited ground state OH radicals:[43b]

$$\begin{array}{ll} O(^1D) + HCl \rightarrow \cdot OH^*(^2\Pi) + Cl(^2P_3/_2) & +\ 45\ \text{kcal.} \\ O(^1D) + H_2O \rightarrow \cdot OH^*(^2\Pi) + OH(^2\Pi) & +\ 29\ \text{kcal.} \end{array}$$

The reaction of $O(^3P)$ with HCl and H_2O is endothermic, and this reaction would not be expected to produce electronically or vibrationally excited OH radicals. In fact, it appears that $O(^3P)$ atoms do not react with H_2O at all, since the addition of water to ozone photolysed by red light, *i.e.*, involving $O(^3P)$, does not affect the decomposition.[46]

Cases in which electronically excited reactants give rise to electronically excited products will not be considered.

D. Characteristics of Chemical Activation.—From the above description of reaction types giving rise to chemical activation some conclusions and deductions regarding the characteristics of chemical activation may be made. It is possible to produce excited molecules which, in suitable cases, contain known amounts of energy. This energy can be varied by utilising different reactions to produce the same molecule. Information about the distribution of the energy of reaction among two or more products can be obtained. In many instances, only molecules in their ground electronic state are involved; the reactions that occur are adiabatic, are well characterised mechanistically, and are readily amenable to comparison with rate theories.

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[60] R. J. Cvetanović, H. E. Gunning, and E. W. R. Steacie, *J. Chem. Phys.*, 1959, **31**, 573.

[61] T. Liu and A. B. F. Duncan, *J. Chem. Phys.*, 1949, **17**, 241.

3. Survey of Occurrence of Chemical Activation

Chemiluminescence.—One of the first phenomena studied[62] which involves chemical activation was bio-chemiluminescence, which is usually associated with enzymic oxidation. The reactions are well characterised only in a few cases.[63,64] Summaries have been given.[65]

Many ordinary oxidations in solution are chemiluminescent.[66,67] Some solid-state reactions, such as decomposition of sodium azide, emit ultraviolet light;[68] many of these systems involve elementary reactions of free radicals and atoms. No example of ultraviolet emission in bio-luminescence has been observed.

Emission has long been observed in gaseous flames. Hydrocarbon–oxygen flames are the most common and have received much experimental attention. The vibrational and rotational distributions of OH in various flames have been measured and in several cases non-thermal equilibrium distribution observed.[69] The mechanism of production of the various species in hydrocarbon flames is largely speculative and, in any case, complex. The luminescent reaction of sodium atoms with halogens,[9,70] and with inorganic[71] and organic[72] halides, are well known and better understood. Detailed discussions of flames have been given.[73,74]

In many cases, emission from a discharge is due to direct electronic excitation. However, in some cases, the emission results from reaction of atoms or molecules in their ground electronic states, as in the nitrogen afterglow;[75] the species responsible appear to include electronically excited nitrogen molecules formed by the combination of nitrogen atoms:[76]

$$\mathrm{M} + \mathrm{N} + \mathrm{N} \rightarrow \mathrm{M} + \mathrm{N}_2{}^{\dagger} \rightarrow \mathrm{N}_2 + h\nu$$

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[62] R. Boyle, *Phil. Trans.*, 1667, **2**, No. 31, 581.

[63] E. H. White, F. McCapra, G. F. Field, and W. D. McElroy, *J. Amer. Chem. Soc.*, 1961, **83**, 2404.

[64] W. D. McElroy and H. H. Seliger, *Scientific American*, 1962, **207**, 76.

[65] E. N. Harvey, "The Nature of Animal Light," J. B. Lippincott, Philadelphia, 1920; "Bioluminescence," Academic Press, New York, 1952.

[66] M. Trautz, *Z. phys. Chem.*, 1905, **53**, 1.

[67] R. Audubert, *Compt. rend.*, 1936, 202, 131, 406.

[68] R. Audubert, *J. Chim. phys.*, 1936, **33**, 507; *Trans. Faraday Soc.*, 1939, **35**, 197.

[69] A. G. Gaydon and H. G. Wolfhard, *Proc. Roy. Soc.*, 1948, **194**, *A*, 169; H. P. Broida, *J. Chem. Phys.*, 1951, **19**, 1383; K. E. Shuler and H. P. Broida, *ibid.*, 1952, **20**, 1389.

[70] H. Beutler and M. Polanyi, *Z. phys. Chem.*, 1928, **1**, *B*, 3; S. v. Bogdandy and M. Polanyi, *ibid.*, 1928, **1**, *B*, 21.

[71] M. Polanyi and G. Schay, *Z. phys. Chem.*, 1928, **1**, *B*, 30; W. Heller and M. Polanyi, *Trans. Faraday Soc.*, 1936, **32**, 633.

[72] C. E. H. Bawn and W. J. Dunning, *Trans Faraday Soc.*, 1939, **35**, 185; E. D. Kaufman and J. F. Reed, *J. Phys. Chem.*, 1963, **67**, 896.

[73] A. G. Gaydon, "The Spectroscopy of Flames," Chapman and Hall, Ltd., London, 1957.

[74] K. E. Shuler, *J. Phys. Chem.*, 1953, **57**, 396.

[75] R. J. Strutt, *Proc. Roy. Soc.*, 1911, **85**, *A*, 219; 1911, **86**, *A*, 56; 1913, **88**, *A*, 539; 1915, **91**, *A*, 303; E. P. Lewis, *Astrophys. J.*, 1900, **12**, 8.

[76] H. Sponer, *Z. Physik*, 1925, **34**, 622; K. R. Jennings and J. W. Linnett, *Quart. Rev.*, 1958, **12**, 116.

Recombination Reactions.—The recombinations of atoms and radicals produce activated products, as in $2H \rightarrow H_2^*$. Recent considerations of the mechanism of recombination of atoms and small molecules[49–51] (discussed above) have had their counterparts much earlier. Some forty years ago, Polanyi[77] and Herzfeld[78] pointed out that atoms only combine if the nascent molecule suffers a collision with a third body which removes some of its energy. Bodenstein[79] supported such "dreirstoss" restriction, since he calculated that triple collisions could adequately account for the reaction rate. This was an alternative to the ideas of Trautz[80] who had proposed an "intermediate complex" in explanation of the third-order reaction between nitric oxide and oxygen.

At sufficiently low pressure the combination of atoms must always be of the second order, the excited molecule being stabilised by emission. This process is many-fold slower than the termolecular collision rate at all normal pressures. Bimolecular second-order recombination of atoms with emission of light has been observed experimentally in favourable cases[81]

$$Br(^2P_{3/2}) + Br(^2P_{1/2}) \rightarrow Br_2(^3\Pi_{0+u})$$
$$Br_2(^3\Pi_{0+u}) \rightarrow Br_2(^1\Sigma_g^+) + h\nu$$

The first mention that combination of *any* two species might not occur unless a third body were present seems to have been made (for hydrogen atom and ethylene) by Taylor and Hill.[82] This idea governed the general conception of methyl and radical recombination for some time.

Energy Chain Theory.—An early theory of unimolecular reactions, by Christiansen and Kramers,[83] used the concept of chemical activation. They suggested that reaction products could carry excess of energy, $E_1 + \Delta H_1$, and activate other reactant molecules by collision. The Boltzmann distribution would thus not be depleted by reaction. The theory, as suggested, failed for several reasons. But distantly related ideas were used some time later to explain isotope exchange,[84] "atom cracking",[7b] and hot-radical[85] reactions. The postulate of energy chains in connection with solid-phase radiation-induced polymerisations has recently been re-introduced by Semenov.[86]

Summary.—The detailed discussion of this section has been confined to some early important systems. That chemically activated molecules and radicals may be important intermediates of reaction is now generally

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[77] M. Polanyi, *Z. Physik*, 1920, **1**, 337.

[78] K. F. Herzfeld, *Z. Physik*, 1922, **8**, 132.

[79] M. Bodenstein, *Z. phys. Chem.*, 1922, **100**, 68.

[80] M. Trautz, *Z. Electrochem.*, 1916, **22**, 104.

[81] H. C. Urey and J. A. Bates, *Phys. Rev.*, 1929, **34**, 1541; G. Herzberg, *Astrophys. J.*, 1939, **89**, 290; H. B. Palmer, *J. Chem. Phys.*, 1957, **26**, 648.

[82] H. S. Taylor and D. G. Hill, *J. Amer. Chem. Soc.*, 1929, **51**, 2922.

[83] J. A. Christiansen and H. A. Kramers, *Z. phys. Chem.*, 1923, **104**, 451.

[84] N. R. Trenner, K. Morikawa, and H. S. Taylor, *J. Chem. Phys.*, 1937, **5**, 203.

[85] B. S. Rabinovitch, S. G. Davis, and C. A. Winkler, *Canad. J. Res.*, 1943, *B*, **21**, 251.

[86] N. N. Semenov, *Pure and Applied Chem.*, 1962, **5**, 353.

recognised. A representative collection (although not complete) of various studies involving chemical activation is given in the Tables of the Appendix. Investigations which explicitly use the features of chemical activation have been made for only about a decade, and it is on a few representatives of these studies that attention will be focused in the remainder of this Review.

4. Specific Studies of Chemical Activation

A. Bimolecular Exchange or Displacement Reactions.—In this type of study, information can be obtained about the nature of the activation reaction. Specifically, for the reaction $P + QR \rightarrow PQ + R$, the relative rates of formation of different vibrational states of the product PQ can be determined.[87] For the reaction $P + QRS \rightarrow PQ + RS$, the vibrational excitation of RS relative to PQ can also be found. Other important aspects of these studies include the nature of collisional deactivation of the excited molecules produced, and the question of promotion of reaction by product molecules due to activation.

Four reactions have been chosen to illustrate these matters.

(*i*) *Reaction between hydrogen atoms and molecular chlorine.* $H + Cl_2 \rightarrow HCl^* + Cl + 45$ kcal.; $E_a \approx 2{\cdot}5$ kcal. This system has been studied in detail by J. C. Polanyi and his co-workers[13,88] at pressures down to 10^{-2} mm./Hg. At the lowest pressure, where collisional deactivation is less important, an observed infrared emission arises from all vibrational levels of HCl up to $v = 5$ (38·1 kcal.). The intensities of the individual rotational lines of various bands of the $\Delta v = 1$ and $\Delta v = 2$ sequences were summed, and the vibrational and rotational population distribution of the HCl molecule was calculated. Now, at thermal equilibrium, the population of the vth level, N_v, is

$$N_v = \frac{N}{Q_v} \exp\left[-G(v)\boldsymbol{hc}/\boldsymbol{k}T\right]$$

where N is the total population, Qv is the vibrational partition function and $G(v)$ is the energy of the vth level. A plot of log (N_v/N_v') against $\boldsymbol{hc}[G(v') - G(v)]$ is a straight line, of slope $1/T$, if vibrational equilibrium exists. If the value of T thus obtained corresponds to the ambient temperature, then equilibrium presumably exists between vibration and translation. Fig. 3 reveals that the HCl molecules produced possess a distinctly non-equilibrium vibrational distribution. Calculation shows that there are appreciable initial rates of formation of HCl into all vibrational states up to $v = 5$, but each rate decreases as v increases.

[87] (*a*) H. S. Heaps and G. Herzberg, *Z. Physik*, 1952, **133**, 48; (*b*) J. D. McKinley, D. Garvin, and M. J. Boudart, *J. Chem. Phys.*, 1955, **23**, 784; (*c*) T. M. Cawthorn and J. D. McKinley, *ibid.*, 1956, **25**, 585; (*d*) F. Kraus, *Z. Naturforsch.*, 1957, **12**, *A*, 479; (*e*) D. Garvin, H. P. Broida, and H. J. Kostkowski, *J. Chem. Phys.*, 1960, **32**, 880; 1962, **37**, 193; (*f*) H. P. Broida, *ibid.*, 1962, **36**, 444.

[88] (*a*) J. K. Cashion and J. C. Polanyi, *J. Chem. Phys.*, 1958, **29**, 455; 1959, **30**, 1097; 1959, **31**, 1338; (*b*) J. K. Cashion and J. C. Polanyi, *Proc. Roy. Soc.*, 1960, **258**, *A*, 529.

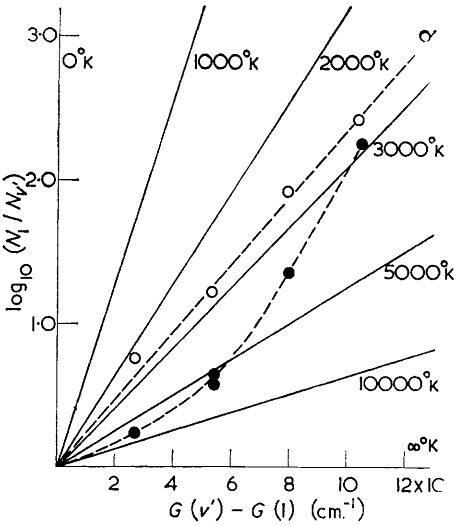

FIG. 3. *Stationary-state distribution among vibrational states of* HCl* *produced by the reaction of hydrogen atoms with chlorine molecules.*

[A Boltzmann distribution of vibrators at the temperatures indicated would give points lying along the solid lines.]

O Represents points obtained at *ca.* 0·2 mm. Hg. (after Cashion and Polanyi, ref. 88*b*).

● represents points obtained at *ca.* 0·02 mm. Hg. (after Charters and Polanyi, ref. 13).

At higher pressures, $\sim 10^{-1}$ mm., the vibrational distribution was found to be of Boltzmann type, with $T = 2700$°K, although, surprisingly, rotational states were not in an equilibrium distribution. The highest vibrational level observed was $v = 6$; the fact that $v = 6$ was not observed at lower pressures suggests that vibration–vibration transitions were important in the work at higher pressure; a ten-fold reduction in pressure reduces collisions of HCl with all other molecules ten-fold, but reduces HCl–HCl collisions by a factor of 100. Vibrational–translational transitions are not efficient and the transition probability $P_{v,v-1}$ is less than 10^{-3}; even if the entire energy of reaction went initially into the HCl molecules, approximately 10^5 collisions do not remove more than 90% of the energy. This follows from the observation that at 1 mm. pressure the HCl molecules were approximately in a Boltzmann distribution equivalent to 3500°K. The total vibrational energy at this temperature is equivalent to 10% of the available energy.

A plot can be made for rotational distributions in vibrational levels, $v = 1$—4, observed at the lowest pressures. It was found that for $J \simeq 1$—7, the rotors in each vibrational level are in thermal equilibrium, which is characterised by the same "temperature" ($\sim$100°C) for all v. For higher J values, the distribution deviates toward those characteristic of higher temperatures. The total excess of energy available from this reaction, $(E_a + \Delta H)$, is $45 + 2{\cdot}5 = 47{\cdot}5$ kcal. There is thus sufficient energy to excite the $J = 20$ rotational level of the $v = 4$ state, which corresponds to 31·2 + 11·7 kcal. The highest observed level (estimated here from plots in the reference) was $J = 17$. Now, HCl molecules suffer approximately 10^3 collisions on the average before emission, and it might be expected that the distribution would have relaxed from its initial value; for low rotational states a change of $\Delta J = 1$ is promoted efficiently by collisions; at high J values, the rotational spacings approach in magnitude the values for vibrational jumps and collisional exchanges may not be as efficient.[89]

It appears probable that the observed rotational distributions are a result of an initial non-Boltzmann equilibrium distribution. On almost every vibrational–vibrational radiative transition, the rotational quantum number will change also; this effect, although small, will tend to maintain a non-equilibrium rotational distribution. At higher pressures, for rotational excitation at the $v = 1$ level (higher vibrational levels did not yield accurate rotational data) a Boltzmann distribution characteristic of room temperature was observed up to $J = 3$. At still higher J values, deviations were observed which corresponded to higher temperatures. The distinct differences in rotational and vibrational distributions in the two sets of work show further that collisional deactivation is an important effect at the pressures studied.

This work admirably demonstrates the presence of chemical activation and the information of various kinds that may be learned about the molecule PQ. To obtain information on the excitation of RS, reactions of the type $P + QRS \rightarrow PQ + RS$ must be investigated.

(*ii*) *Reaction between hydrogen atoms and nitrosyl chloride.* Although reactions such as $H + O_3 \rightarrow OH + O_2$[87] and $O + NO_2 \rightarrow NO + O_2$[90] have been examined, selection of the present system is desirable for several reasons. This reaction has been studied by Cashion and Polanyi[91] in the same manner as the earlier investigations of $H + Cl_2$ at higher pressures. Both product molecules are heteronuclear, and infrared-active, and may readily provide information regarding the excitation of the released species, NO, as well.

Cashion and Polanyi concluded that the major infrared emission resulted from the reaction

$$H + NOCl \rightarrow HCl^* + NO \quad + 65 \text{ kcal.}$$

Emission consisted of the fundamental, first, and second overtone vibrational sequences of the electronic ground state of HCl. The highest vibrational level definitely observed ($v = 9$) is 63·6 kcal. above the zero state. Although the $v = 9$ and lower states may have arisen from vibra-

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[89] T. L. Cottrell and J. C. McCoubrey, "Molecular Energy Transfer in Gases," Butterworths, London, 1961; K. F. Herzfeld and T. A. Litovitz, "Absorption and Dispersion of Ultrasonic Waves," Academic Press, New York, 1959.

[90] (*a*) F. J. Lipscomb, R. G. W. Norrish and B. A. Thrush, *Proc. Roy. Soc.*, 1956, **233**, *A*, 455; (*b*) R. A. Kane, J. J. McGarvey, and W. D. McGrath, *J. Chem. Phys.*, 1963, **39**, 840.

[91] J. K. Cashion and J. C. Polanyi, *J. Chem. Phys.*, 1961, **35**, 600.

tional–vibrational energy transfer, as occurred in the $H + Cl_2$ system at similar pressures, the initial distribution is definitely a non-equilibrium one. The calculation made in this paper of the relative rates of chemical reaction into each vibrational level may be somewhat in error, but probably not the semi-quantitative conclusion, that the relative rates of formation into each decreases as v rises. Such behaviour may not be general, however.[48]

Emission was also observed from vibrationally excited NOCl ($v = 1,2$) and a weak emission from vibrationally excited NO ($v = 1$). Emission from NO* was approximately one-tenth that of HCl under all flow conditions. This suggests that the production of excited RS is not an important process.

Because the NO and HCl emissions varied in a similar manner with conditions, they may well be formed by the same chemical reaction. Excitation of NO (and of NOCl) by a collisional process, whilst acting as deactivators, may also have occurred.

The rotational level distribution for HCl could be described as an equilibrium distribution at a temperature of 1970°K, except for the first three rotational states which corresponded to a much lower effective temperature.

(iii) Reaction of oxygen atoms with chlorine dioxide. The use of infrared emission in these studies suffers from the restriction that the emitting species undergoes 10^3—10^6 collisions before emitting. The measurement of absorption spectra immediately after the formation of a species can yield more direct information on the initial energy distribution. Measurements at progressively longer delay times then give rates of relaxation of the excited species.

Such a technique, developed by Norrish and his co-workers, has been applied to the reaction of $O(^3P)$ atoms with ClO_2:[90]

$$O(^3P) + ClO_2 \rightarrow O_2^* + ClO \qquad + 61 \text{ kcal.}$$

Flash photolysis of ClO_2 was used to produce the O atoms;

$$ClO_2 + h\nu \rightarrow ClO + O$$

The vibrationally excited O_2 was studied by means of the Schumann–Runge absorption between 2200 and 2600 Å. The photolyses were carried out with 250 to 3000-fold excesses of inert gases present. Decay of ClO and of excited O_2 was measured at varying delay times. In all experiments, the maximum concentration of excited O_2 was observed at the shortest delay time (10 μsec.) after the beginning of the photolytic flash. This time is shorter than the radiative lifetimes of excited O_2, since dipole emission is forbidden and only magnetic dipole or quadrupole emission occurs. The vibrational distributions for O_2 levels below $v = 5$ could not be measured. In levels $v = 5$, 6, and 7, it appeared that approximately equal numbers of molecules were present, but appreciably less in $v = 8$, the highest level observed (34 kcal.). Rotational distributions could not be accurately measured, but appeared to follow a Boltzmann distribution corresponding to the ambient room temperature.

The excitation of ClO was difficult to detect owing to the small dispersion of its spectrum.

Measurements of the half-life of excited O_2 were made with different inert gases. For higher levels the half-lives were slightly shorter, and those for the lower ones slightly longer. The number of collisions required to deactivate the $v = 6$ level were calculated from the data (Table 2).

TABLE 2. *Collisional deactivation efficiencies for* $O_2^*(v = 6)$

Deactivation species	*Number of collisions for deactivation*	*Near vibrational frequencies* (cm.$^{-1}$)
N_2	$>10^7$	2359
CO_2	7000	1286, 1388
ClO	2000	868
ClO_2	~2000	945, 1106
Ar	$>10^7$	——
——	——	——
O_2 frequency intervals	7 to 6	1417
	6 to 5	1440

Included in Table 2 are the vibrational frequencies nearest to the $\Delta v' =$ 7—6 and 6—5 intervals. Removal of energy evidently occurs most readily for near-resonance of the energy levels.

The analysis of relaxation data in terms of half-lives becomes complex when more than two levels are involved in the relaxation process;[92] it is necessary to follow the relaxation of several, and preferably all, energy levels. Basco and Norrish[93] have shown, however, that for systems in which the vibrational populations decrease towards higher levels, and where the change of relative populations is small over one or two apparent half-lives, measurement of the changes in relative populations can provide accurate relaxation data. On applying this to the $O + ClO_2$ reaction, where the half-lives of $v = 5$, 6, and 7 levels were not greatly different, it was found that the fifth, sixth, and seventh levels were probably populated to a decreasing extent, but that the relaxation results may not be in error by more than a factor of two.

(iv) Reaction of nitrogen atoms with nitric oxide. The reaction of N atoms with NO in the presence of ozone may provide a case[45b,c] where the further reactivity of the chemically activated product is promoted:

$$N + NO \rightarrow N_2^* + O \qquad + 75 \text{ kcal.} \qquad (d)$$

Reaction (*d*) is faster ($k = 2{\cdot}2 \times 10^{-11}$ cm.^{3} molecule^{-1} sec.$^{-1}$) than subsequent reactions between NO and N with O:

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[92] K. E. Schuler, *J. Phys. Chem.*, 1957, **61**, 849.
[93] N. Basco and R. G. W. Norrish, *Discuss. Faraday Soc.*, 1962, **33**, 99.

$$NO + O + M \rightarrow NO_2 + M \qquad (e)$$
$$NO + O \rightarrow NO_2 + h\nu \qquad (f)$$
$$N + O + M \rightarrow NO + M + h\nu \qquad (g)$$

In the presence of excess of N atoms or NO, chemiluminescence results [reactions (*f*) and (*g*)]. When reaction (*d*) occurs between stoicheiometric amounts of N and NO the reaction is non-chemiluminescent, and (*h*) may be studied without interference from (*f*) and (*g*):

$$N_2^* + O_3 \rightarrow N_2 + O_2 + O \qquad (h)$$

Vibrational excitation from reaction (*d*) was first suggested by Kaufmann and Kelso.[45a] Morgan, Phillips, and Schiff[45c,d] carried out a calorimetric investigation and determined that the average energy of the chemically-produced nitrogen molecules is 21 ± 5 kcal. mole^{-1}, *i.e.*, substantially below the exothermicity. Phillips and Schiff,[45b] on investigating the reaction of active nitrogen with ozone, observed that the addition of nitrous oxide (an efficient deactivator of vibrationally excited nitrogen) reduced the decomposition of the ozone. They suggested that nitrogen molecules were produced with sufficient energy ($> 23{\cdot}4$ kcal. mole^{-1}) to decompose ozone. This conclusion has been supported by later work[45c] in which N atoms were titrated with nitric oxide. Ozone was also added and its rate of consumption was determined. In this way, the percentage of nitrogen molecules formed with energy equal to or greater than 23·4 kcal. ($v > 4$) was evaluated as 62—75%. Comparison of this percentage with the results from the calorimetric study indicated that nitrogen molecules are produced with a non-Boltzmann distribution of energies having a maximum population near $v = 4$.

The rates of collisional deactivation of excited nitrogen molecules by N_2 and N_2O were also obtained ($k = 3{\cdot}5 \times 10^{-16}$ for N_2; $k = 1{\cdot}3 \times 10^{-15}$ cm.^{3} molecule^{-1} sec.$^{-1}$ for N_2O) by the titration of N_2^* ($v > 4$). It is of interest to compare the collisional efficiency of nitrogen molecules for deactivation of N_2^* below $v = 4$, as measured chemically, and the efficiency for degradation of vibrational into translational energy, as measured calorimetrically. The latter efficiency is estimated as some fifty times lower than the former. This fits in with theoretical considerations that, because of the matching of the energy levels of nitrogen, resonance transfer would be expected to be very efficient; also, the Landau–Teller theory predicts inefficient conversion of vibrational energy into translation.[89]

B. Bimolecular Association Reactions.—The principal features of systems involving bimolecular association reactions [Section 2B, type (iii)] will be illustrated in detail in terms of two examples chosen from a number of similar reactions (Appendix, Table *B*): these are the addition of H atoms to alkenes to give radicals, and the reactions of methylene radicals with alkenes to produce hot molecules.

(*i*) *Reaction of hydrogen atoms with butene.* The reaction of H atoms with but-1-ene and but-2-ene has been investigated in detail by Rabinovitch and his co-workers, with use of a diffusion flame type of experimental arrangement,[19,94]

$$H + C_4H_8 \rightarrow s\text{-}\dot{C}_4H_9^*;\ E_a \approx 2\ \text{kcal. mole}^{-1} \qquad (i)$$

The collision yield for H addition to the double bond is approximately 10^{-3}. The chemical relaxation time is therefore much longer than momentum relaxation times, and a Boltzmann distribution of reactants is maintained. The effect of multiple isotopic deuterium substitution of butene has also been investigated.[94a]

Variation of energy of the activated radical. The energy of the activated radical may be varied by starting with *cis*- or *trans*-but-2-ene or with but-1-ene, and by adding either hydrogen or deuterium atoms. The thermochemistry of these systems is quite well known. Some average internal energy parameters of s-butyl radicals formed in the various ways are given in Table 3. Since the activation energy for reaction (*i*) is small, the system can be studied at —78°C, as well as at 25°C, which reduces both the energy spread of the radicals and their average energy.

Dependence of rates of decomposition on energy. The activated s-butyl radical may undergo the following reactions

$$s\text{-}\dot{C}_4H_9^* \xrightarrow{k'_E} C_4H_8 + H \qquad (j)$$

$$\xrightarrow{k_E} \cdot CH_3 + C_3H_6 \qquad (D) \qquad (k)$$

$$\xrightarrow{\omega} s\text{-}\dot{C}_4H_9 \qquad (S) \qquad (l)$$

TABLE 3. *Energy (kcal. mole^{-1}) of excited s-butyl and* [$^2H_1$] *butyl radicals in various systems.*

System	Min. energy $E_{min.} = E_1 + \Delta H_1$	Min. excess energy‡ $E^+_{min.} = E_{min.} - E_0$	Average excess energy of formed radicals ⟨E⁺⟩	
			—78°C	25°C
H + *trans*	38·7	5·7	7·2	8·6
H + *cis*	40·0	7·0	8·5	9·9
H + but-1-ene	41·1	8·1	9·6	11·0
D + *trans*	40·5	7·5	9·0	10·5
D + *cis*	41·8	8·8	10·3	11·8
D + but-1-ene	42·9	9·9	11·4	12·9

‡Refers to reaction (*k*) in the text.

Since reaction (*j*) is the reverse of the formation reaction (*i*), $E^+_{min.} = 0$ and $<E^+>$ is only a few kilocalories for this process. The lifetime of an

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[94] (*a*) J. W. Simons, D. W. Setser, and B. S. Rabinovitch, *J. Amer. Chem. Soc.*, 1962, **84**, 1758; (*b*) B. S. Rabinovitch, R. F. Kubin, and R. E. Harrington, *J. Chem. Phys.*, 1963, **38**, 405.

activated species depends on its complexity and on its excess of energy. For the former reason, as comparison with the H + C_2H_4 system shows,[20] and for the latter reason as shown by calculation,[94b] reaction (*j*) is negligible compared with the decomposition (*k*), for which $E^+_{\text{min.}}$ is 6—10 kcal. mole^{-1} (Table 3). An alternative fate of the activated radical is collisional deactivation. The relative amounts of stabilisation, *S* (reaction *l*), and decomposition, *D* (reaction *k*), of the activated radicals are measured as a function of pressure.

This system provides well-controlled conditions and furnishes a clear test of unimolecular reaction theory, and the predicted variation of rate with excitation energy.

Since the radicals are formed with some energy spread, the measured rate constant is not k_E but an average rate constant, defined as $k_a = \omega{\cdot}D/S$. This is related to k_E as follows:

$$k_a = \omega{\cdot}D/S = \omega\frac{\int_{E_{\text{min.}}}^{\infty}\frac{k_E}{k_E + k_E' + \omega}f(E)\,\mathrm{d}E}{\int_{E_{\text{min.}}}^{\infty}\frac{\omega}{k_E + k_E' + \omega}f(E)\,\mathrm{d}E} \tag{4}$$

where $f(E)$ is given by eqn. (1); k_E' is negligible and can be neglected. The limiting high and low pressure forms which this equation takes are $k_{a\infty} = \langle k_E\rangle$, and $k_{a0} = \langle 1/k_E\rangle^{-1}$. The ratio $k_{a\infty}/k_{a0}$ provides a measure of the effective energy spread or dispersion described by $f(E)$, and is unity for monoenergetic activation; this ratio for butenes was found to be less than 2 at 25°C, and less than 1·3 at −78°, which is orders of magnitude smaller than the comparable ratio, *i.e.*, energy dispersion, for thermal activation. This demonstrates the relatively monoenergetic character of the excited butyl radicals, especially at −78°C.

The Marcus–Rice[3b,95] form of k_E has been used to calculate theoretical values of $k_{a\infty}$ and k_{a0}, for each system. This involves the computation of k_E on a quantum statistical, rather than classical, basis. Good agreement of both absolute rate magnitudes and their variation with energy was obtained between observed and calculated values (Fig. 4) of $k_{a\infty}$ and k_{a0}. This supports the validity of the Marcus–Rice (RRKM) model for the calculation of unimolecular reaction rates, and the postulate of the theory regarding efficient intramolecular relaxation of energy between the active degrees of freedom of the molecule. This agreement was found for these systems, and others,[4] only when *all* vibrational and internal rotational degrees of freedom were taken as active, together with those overall rotations which interact with vibrational motions. These activation systems thus assist materially in establishing the best detailed *a priori*

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[95] R. A. Marcus and O. K. Rice, *J. Phys. Colloid Chem.*, 1951, **55**, 894.

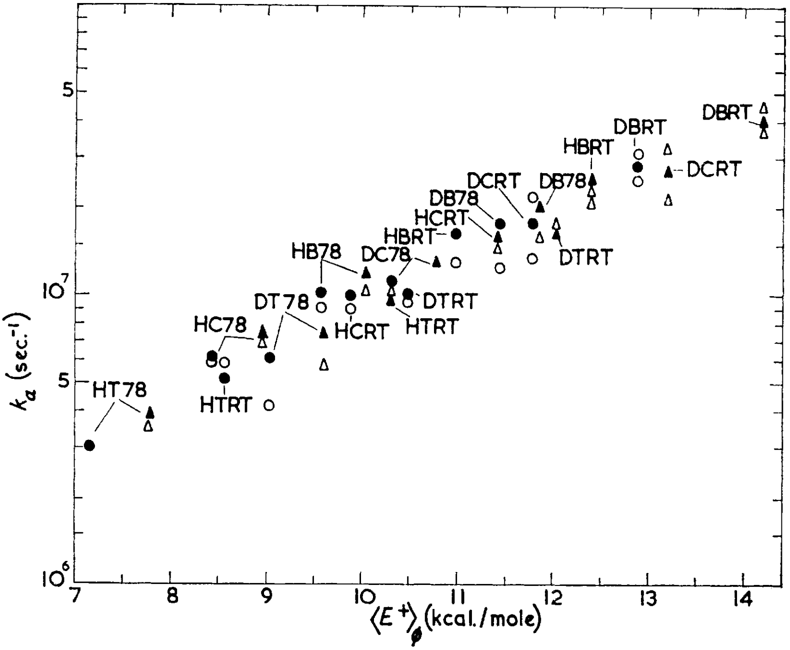

FIG. 4. *k_a as a function of $\langle E^+\rangle_\phi$, the average energy of the reacting radicals.* Observed values: O, $p = 0$; Δ, $p = \infty$; calculated values, filled symbols. The system designation employs the letters H or D for the atom used, B, C, T for but-1-ene, *cis*- and *trans*-but-2-ene reactant, 78 for —78°C (195°K) and RT for 27°C (300°K). The relation between observed and calculated values is a vertical one in the Figure (taken from ref. 97).

theoretical model for the calculation of unimolecular reaction rates. Predictive tests, *e.g.*, predicted and measured secondary isotopic rates for [$^2H_8$]butyl from H + [$^2H_8$]*cis*-but-2-ene, have also supported the theory.[94a]

An interesting confirmation of the occurrence of internal energy randomisation is provided by a comparison of the behaviour of the s-butyl radical formed from but-2-ene (H atom addition to a non-terminal carbon atom is followed by rupture of the attached C–C bond),

$$\mathrm{H + C{-}C{=}C{-}C \rightarrow C{-}C{-}\underset{\underset{\mathrm{H}}{|}}{C}{\not-}C}$$

and from but-1-ene (addition is to the terminal carbon atom and rupture of the most remote C–C bond takes place),

$$\mathrm{H + C{-}C{-}C{=}C \rightarrow C{\not-}C{-}\underset{\bullet}{C}{-}CH}$$

On initial formation, the excess of energy is obviously distributed in different ways in these two cases. The fact that the radicals in both preparations decompose at comparable rates[96] means that the relaxation time for internal energy migration is less than that for decomposition.

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[96] R. E. Harrington, B. S. Rabinovitch, and H. M. Frey, *J. Chem. Phys.*, 1960, **33**, 1271.

Intermolecular energy transfer. The butyl radical system has also been used for the measurement of collisional transition probabilities.[97a] The effect of the addition of various inert gases on the value of k_a for s-butyl was studied. The principle of the experiment assumes a very simple form in these non-equilibrium systems: radicals are formed directly without collisional activation, having energy in excess of $E_{\min.}$ (Fig. 5); if they experience an energy cascade on collision, rather than efficient deactivation below the critical level E_0 on each collision, they may undergo further decomposition at each successive level entered above E_0; the ratio of S/D, especially at low pressures, is sensitive to the details of the vibrational cascade, *i.e.*,

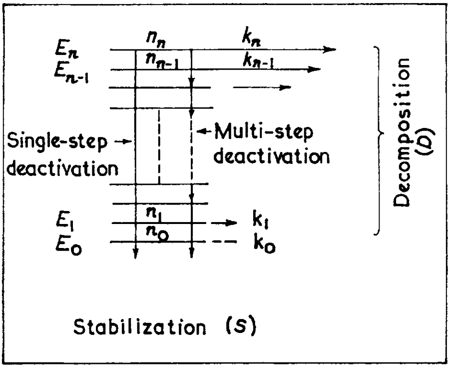

FIG. 5. *Representation of decomposition and stabilisation processes for a model system with activation at level* $E_n \equiv E_{min}$. (taken from ref. 94*b*).

$$(D/S)_n = (1/\beta\omega)^n \prod_{i=1}^{n} (\beta\omega + k_i) - 1 \qquad (5)$$

where β is the effective collision factor, ω is the collision frequency, n is the number of transitions in the active region, and k_i refers to the specific rate of decomposition at each intermediate energy level.

The average amount of energy removed per collision by the rare gases and diatomic molecules H_2, D_2, N_2, was found to be 1·2—3 kcal. mole^{-1}. The average energy transferred per collision to poly-atomic deactivators such as butene, SF_6, CH_3Cl and CD_3F was >9 kcal. mole^{-1}, with intermediate values of 5 kcal. mole^{-1} found for smaller molecules such as CO_2 and CH_4; collisional deactivation cross-sections conform well to the Lennard-Jones potential. Energy transfer even to rare-gas atoms and small molecules is thus surprisingly efficient ($\langle \Delta E \rangle > kT$). Refined measurement can also lead to information about the form of the collision transition probabilities as a function of energy; this is the problem ahead.

The collisional deactivation efficiencies of the rare gases increases some-

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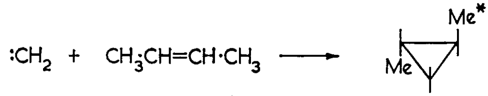
[97] (*a*) G. H. Kohlmaier and B. S. Rabinovitch, *J. Chem. Phys.*, 1963, **38**, 1692, 1709; (*b*) D. W. Setser, B. S. Rabinovitch, and J. W. Simons, *J. Chem. Phys.*, 1964, **40**, 1751.

what with increasing atomic weight and with decreasing bath temperature. The theories of Landau and Teller, and of Schwartz, Slawsky, and Herzfeld,[89] for energy exchange, applied usually to the collisions of diatomic or small molecules at low energies as mentioned earlier, predict much smaller probabilities for the transfer of such large amounts of energy, a positive temperature coefficient, and a decreased efficiency with increase in mass. These items are contrary to the findings in the activated s-butyl[97] and ethyl radical[20] systems. These theories may not be used to predict the extent of energy exchange between polyatomic molecules at high energies.

(*ii*) *Reaction of methylene with but-2-ene.* The reaction of singlet methylene with olefins and alkanes gives rise to an energised molecule, which then undergoes a variety of non-radical reactions. The reaction of methylene with *cis*- and *trans*-but-2-ene has been studied in greatest detail, by Frey[18] and by Setser and Rabinovitch.[32] Methylene was produced by the photolysis (4100 Å) and thermal decomposition of diazomethane, and by photolysis of ketene at various wavelengths centered at 3100 Å. The addition to the double bond is stereospecific; *trans*-but-2-ene gives excited *trans*-1,2-dimethylcyclopropane initially,



This is characteristic for reactions of singlet methylene.[98] The excited dimethylcyclopropane has more than sufficient energy to react and gives the same products that are formed in the thermal isomerisation of 1,2-dimethylcyclopropane (Sec. 2*B*) for which $E_0 \sim 60$ kcal. mole^{-1}. Methylene insertion into carbon–hydrogen bonds gives rise directly to 2-methylbut-2-ene and *trans*-pent-2-ene:

$$:CH_2 + trans\text{-}CH_3\cdot CH{=}CH\cdot CH_3 \left.\vphantom{\begin{array}{l}a\\b\end{array}}\right\} \begin{array}{l} \rightarrow trans\text{-}CH_3\cdot CH{=}CH\cdot CH_2\cdot CH_3{}^* \\ \rightarrow CH_3\cdot CH{=}C(CH_3)CH_3{}^* \end{array}$$

Energy variation of activated dimethylcyclopropane. The methylene is invariably produced with an ill-defined excess of vibrational energy. The relative magnitude of this excess may be varied by 5—10 kcal. by pyrolysis of diazomethane at different temperatures, or photolysis at different wavelengths of the photolysing light. From experimental evidence of the effect of inert gases on the reaction, it appears[18] that methylene radicals may have excess of translational energy, arising from their genesis, which is removed after a few collisions with inert-gas molecules.

The yield of the stabilised dimethylcyclopropane increases with pressure as exp($-$constant/p), when p is sufficiently large, and tends to a limiting value. This value is independent of the mode of formation of methylene, but the yield at lower pressures varies with the mode of formation. This

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[98] P. S. Skell and R. C. Woodworth, *J. Amer. Chem. Soc.*, 1956, **78**, 4496.

reflects the different excesses of energy carried by methylene. A plot for *trans*-but-2-ene as initial reactant, of the form, $y = b + mx$, *i.e.*,

$$\frac{trans\text{-DMC}}{cis\text{-DMC}} = \frac{k_{cis \rightarrow trans}}{k_{trans \rightarrow cis}} + \frac{1}{k_{trans \rightarrow cis}} \cdot \frac{\omega(D + S)}{S} \tag{6}$$

is found to be a straight line; S refers to total stabilised dimethylcyclopropane. The reciprocal of the slope gives the rate of geometrical isomerisation of activated *trans*- dimethylcyclopropane. Since this value is found to be constant (differing for different sources of methylene, however) it follows that the activated molecules are formed in a distribution that is closely monoenergetic.

The average lifetime of thermally activated dimethylcyclopropane molecules reacting (average energy ~79 kcal. mole^{-1}) is ~10^{-6} sec.,[29,99] as compared with the chemically activated species (average energy ~110 kcal. mole^{-1}) which has an average lifetime of ~10^{-8} sec.

The molecules formed by carbon–hydrogen insertion reactions also possess sufficient energy to undergo further reaction at low pressures. Thus

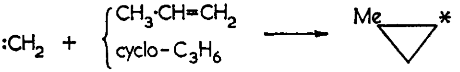
$$cis\text{-pent-2-ene}^* \rightleftharpoons trans\text{-pent-2-ene}^*$$

and

$$cis\text{-pent-2-ene}^* \rightarrow \text{decomposition products}$$

Relation to reaction theory. Application of a theoretical formulation to the unimolecular isomerisation rate of the excited dimethylcyclopropane has been made in a manner similar to that described for the butyl system.[32] Since the total energy is not known *a priori*, the theoretical calculations were reversed: a value of the energy (~105—110 kcal. mole^{-1}) was found which gave the best fit of the calculated values to the experimental k_a. The method has been used to find the fraction of excess photolysis energy retained by ethylene on photolysis of ketene (50—85%) and diazomethane (30—50%).[32]

Mention should be made of another system. Butler and Kistiakowsky[100] produced energised methylcyclopropane by reaction of methylene with propylene or cyclopropane:



The difference in energy content of the methylcyclopropane formed by these reactions is known to be 7·9 kcal. mole^{-1}. The experimental rate ratio found for the two systems was 3·8. The theoretical formulation is in good agreement: this energy increment is predicted[32] to cause an increase in rate of approximately 3·4.

Comparison of the two modes of production of methylcyclopropane

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[99] M. C. Flowers and H. M. Frey, *J.*, 1962, 1157.
[100] J. N. Butler and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1960, **82**, 759.

and the proportions of butene structural isomer products demonstrates, as pointed out by Butler and Kistiakowsky, that intramolecular energy transfer must be more rapid than the rates of reaction of the energised molecules.

Studies of energy transfer. The effect of added inert gases on the rate of deactivation of the excited cyclopropane species in methylene systems has been studied.[18,101] Use of added oxygen removes any effects due to the collisional conversion of singlet methylene into the ground triplet state.[102] Large amounts of energy ($\sim$10—20 kcal. mole^{-1}) on the average are removed, per collision on deactivation of cyclopropane by ethylene, and of dimethylcyclopropane by butene (Table 4); the inert gases helium and argon have less, but fairly high efficiency (0·15—0·3 on a pressure basis).

TABLE 4. *Deactivation of various cyclopropanes.*[97b]
$\langle E\rangle \sim 105$ kcal. mole^{-1}; $E_0 \sim 60$ kcal. mole^{-1}.

Species	Deactivator	Average energy decrement per collision‡					
		450°	400°	325°	300°	150°	25°
Dimethylcyclopropane	butene		10		12		
Methylcyclopropane	cyclopropane						$\geqslant$30¶
Cyclopropane	ethylene	7		10		12	10—30‖

‡Calculated on the basis of a simple step-ladder energy cascade model; other models do not alter the average decrement appreciably.
¶Estimated from the data of reference 101*b*.
‖Conflicting estimates from reference 97*b* and unpublished data of J. W. Simons.

5. Summary

Bimolecular activation reactions offer the most useful and potentially fruitful systems, although the study of the recombination of atoms has also been of great value.[1]

A. Bimolecular Exchange Reactions.—The systems discussed previously are fairly complex even though they involve small molecules and some interpretations are probably subject to change. Nonetheless, in general, the following conclusions apply.

PQ product molecules may be vibrationally excited up to the maximum possible value, but when P is an H atom, and in some cases when it is heavier,[90b] entry into lower vibrational states is favoured. The level of excitation has been discussed by Basco and Norrish;[43a] it follows, more or less, the earlier mentioned theories of Polanyi,[3] Smith,[47] and Bunker.[48]

The significance of this for the reverse reaction of the product PQ is that vibrational excitation of these species, as reactants, may enhance reactivity;

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[101] (*a*) H. M. Frey and G. B. Kistiakowsky, *J. Amer. Chem. Soc.*, 1957, **79**, 6373; (*b*) J. N. Butler and G. B. Kistiakowsky, *ibid.*, 1961, **83**, 1324; (*c*) D. W. Setser, J. W. Simons, and B. S. Rabinovitch, *Bull. Soc. chim. belges*, 1962, **71**, 662.

[102] H. M. Frey, *J. Amer. Chem. Soc.*, 1960, **82**, 5947.

but the favoured path in reaction phase space, at least when P is a light atom, and in some cases when it is not, is the one which has usually been assumed in bimolecular processes, namely, that involving a high degree of excitation of relative motion of the reaction partners. Exceptions occur: enhanced cross-section for excitation of the $v = 4$ state of OH* in the reaction[87c,e]

$$H + O_3 \rightarrow O_2\dagger + OH^*$$

corresponds to resonance excitation of $O_2(^1\Sigma_g^+)$. This implies a special efficiency of the reverse process at this level of vibrational excitation of OH.

Blais and Bunker[48] have calculated the behaviour expected in these types of systems for particular interaction potentials. For certain conditions, PQ is highly excited if P is heavy.

RS is not highly excited, as based on the evidence from the reaction of H atoms with NOCl. In other reactions of this type, little or no evidence has been obtained for excitation of RS. This is also in accord with the previously mentioned theories.

Vibration–vibration energy transfer collisional transition probabilities may be measured, and have been found to be relatively high, especially at near-resonance. Vibration–translation and rotation–translation probabilities may also be determined. The results for small molecules support the predictions of the Landau–Teller theory, and variants thereof.[89] These studies provide a valuable and direct method for obtaining information about specific collision-induced transitions.

Reactivity of products may be enhanced as a consequence of their excitation, but to date this is not a well-established or important phenomenon.

Various future studies of many types would be useful. Enough data for good test of theory of reaction are not even available for the system P + QR. The careful study of more systems of the type P + QRS, with production of RS would be useful in order to provide more information regarding the reaction hypersurface in such systems. The study of the deactivation efficiencies of inert gases for a molecule in various vibrational states (*e.g.*, the deactivation of O_2^* which may be produced in different energy distributions using different activation reactions) would be valuable.

B. Bimolecular Association Reactions.—These systems provide a method of forming excited species with very small dispersion of energy. The minimum excess of energy $E^+_{\text{min.}}$ may be varied, depending upon whether or not the same bond is broken in reaction as is formed in activation. Thus, for the system

$$H + C_2H_4 \rightleftharpoons \cdot C_2H_5^*,\ E^+_{\text{min.}} = 0$$

the same bond is broken. While for the reaction

$$H + CH_3\cdot CH{=}CH\cdot CH_3 \rightarrow s\ {-C_4H_9} \rightarrow \cdot CH_3 + C_3H_6,$$
$$E^+_{\text{min.}} = 7\ \text{kcal. mole}^{-1}$$

a different bond is broken; $E^{+}_{\text{min.}}$ is a function of the two bonds involved, thus

$$H + CH_3{\cdot}CH{=}CH{\cdot}CH_2Br \rightarrow CH_3{\cdot}CH_2{\cdot}\dot{C}H{\cdot}CH_2Br^{*} \rightarrow \text{but-1-ene} + Br,$$

$$E^{+}_{\text{min.}} \sim 25 \text{ kcal. mole}^{-1}$$

Considerable flexibility of energetics and bond type is possible in such systems.

Where more than one type of bond rupture may occur, comparative dissociation processes may be accurately studied:

$$\begin{aligned} &H + C{-}C{-}C{=}C{-}C{-}C \rightarrow C{-}C{-}\dot{C}{-}C{-}C{-}C \rightarrow \dot{C} + C{=}C{-}C{-}C{-}C \\ &\text{or} \qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad \rightarrow C{-}\dot{C} + C{=}C{-}C{-}C \end{aligned}$$

Dainton[103] has summarised some of the useful characteristics of chemical activation techniques.

A Marcus–Rice model for the calculation of unimolecular reaction rates, coupled with the assumption that all vibrational and internal rotational degrees of freedom are active, has been found to yield good agreement with experiment. Following from this is the conclusion that intramolecular energy relaxation in highly excited anharmonic species is very rapid. These systems are well adapted to detailed study of isotope and quantum-statistical effects. Careful studies should yield information on the nature of the distribution of collisional transition probabilities. The assumption of unit collisional deactivation efficiency in the case of complex molecules may not be much in error for practical purposes. This activation technique possibly provides the best experimental conditions for the study of energy transfer by highly vibrationally excited complex species; they complement the information that can be obtained for small radicals and molecules from exchange reaction systems.

This work was supported by the U.S. Office of Naval Research.

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APPENDIX

TABLE A. *Unimolecular isomerisations and decompositions.*

Reaction	Activation with respect to:	Evidence for chemical activation	Refs.‡
1 Methylcyclopropane → butenes*	*cis-trans* Isomerisation of but-2-ene		*28*
2 *cis*- → *trans*-1,2-Dimethylcyclopropane*	Reverse reaction	♯	*29*
→ pentenes*	Structural isomerisation	♯	*29*
3 *cis*- → *trans*-1,2-Dimethylcyclobutane*	Reverse reaction	♯	*30*
4 *cis*-olefin → *trans*-olefin*	Reverse reaction	♯	*16, 26*
5 *cis*-RN=NR → *trans*-RN=NR*	Reverse reaction	♯	*27*
6 $N_3H \rightarrow NH\dagger(^3\Pi) + N_2$	Emission	emission from $NH(^3\Pi)$	*33*
7 Dimethyldiazirine → Me_2C:* + N_2	Rearrangement to $CH_3CH{=}CH_2$	proposed mechanism	*34*
8 Ethylene oxide → $CH_3{\cdot}CHO$*	Decomposition of acetaldehyde	decomposition products	*104*

‡ Italicised references in the Appendix refer to citations in the main text.

♯ Cases where it would be predicted that further reaction would occur if reaction were carried out at sufficiently low pressure.

TABLE B. *Bimolecular combinations.*‡

Reactions§		$-\Delta H^{\#}$ (kcal./mole)	Evidence for chemical activation	Reactions of activated molecule (other than deactivation or reverse reaction)	Refs.
1	$H + O_2 \rightarrow HO_2^*$	47	Decomposes unless deactivated (d.u.d.). I.r. emission		1
2	$H + \cdot OH \rightarrow H_2O^*$	118	d.u.d. Electronic excitation of sodium, lead and thallium		55, 2
	$H + \cdot OH \rightarrow H_2O + h\nu$	118	Either radiative combination or emission from H_2O		3
3	$H + NO \rightarrow HNO†$ $\rightarrow HNO^*$	49	d.u.d. Emission in red and i.r.		4
4	$H + RNH \rightarrow RNH_2^*$	85	d.u.d.	Decomposition, e.g. $C_2H_5{\cdot}NH_2^* \rightarrow \cdot C_2H_5 + \cdot NH_2$ $\rightarrow \cdot CH_3 + \cdot CH_2{\cdot}NH_2$ $\rightarrow C_2H_5N + H_2$	5
5	$H + \cdot CH_3 \rightarrow CH_4^*$	102	d.u.d. Deuterium exchange		6

‡ Isotopic labelling is not specifically designated but was used in many cases cited.

§ Reactant atoms are in ground electronic state, unless otherwise indicated.

Approximate heat of reaction; E_1 must be added to obtain level of activation of products.

[1] (*a*) D. E. Hoare and A. D. Walsh, *Trans. Faraday Soc.*, 1957, **53**, 1102; (*b*) L. I. Avramenko and R. V. Kolesnikova, *Proc. Acad. Sci. U.S.S.R.* (*Phys. Chem.*), 1961, **140**, 750; R. R. Baldwin and C. T. Brooks, *Trans. Faraday Soc.*, 1962, **58**, 1782; R. N. Dixon and B. F. Mason, *Nature*, 1963, **197**, 1198.

[2] (*a*) O. Oldenberg and F. F. Rieke, *J. Chem. Phys.*, 1939, **7**, 485; E. M. Bulewicz and T. M. Sugden, *Trans. Faraday Soc.*, 1958, **54**, 1855; (*b*) P. J. Padley and T. M. Sugden, *Proc. Roy. Soc.*, 1958, **248**, *A*, 248.

[3] P. J. Padley, *Trans. Faraday Soc.*, 1960, **56**, 449.

[4] J. K. Cashion and J. C. Polanyi, *J. Chem. Phys.*, 1959, **30**, 317; M. J. Y. Clement and D. A. Ramsay, *Canad. J. Phys.*, 1961, **39**, 205; M. A. A. Clyne and B. A. Thrush, *Trans. Faraday Soc.*, 1961, **57**, 1305, *Discuss. Faraday Soc.*, 1962, **33**, 139; R. Simonaitis, *J. Phys. Chem.*, 1963, **67**, 2227; O. P. Strausz and H. E. Gunning, *Trans. Faraday Soc.*, 1964, **60**, 347.

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[6] R. Berisford and D. J. LeRoy, *Canad. J. Chem.*, 1958, **36**, 983.

TABLE B.—*continued*

Reactions§	$-H^{\#}$ (kcal./mole)	Evidence for chemical activation	Reactions of activated molecule (other than deactivation or reverse reaction)	Refs.
6 $H + \cdot C_2H_5 \rightarrow C_2H_6^*$	98	d.u.d.	$\rightarrow 2 \cdot CH_3$	*7*, *8*, 7
7 $H + i\text{—}C_3H_7 \rightarrow C_3H_8^*$	93	d.u.d.	$\rightarrow CH_3CH_2 + \dot{C}H_3$	*7a*, 8
8 $H + C_2H_4 \rightarrow \cdot C_2H_5^*$	38	*cis-trans*-Isomerisation of [$^2H_2$] ethylene. Hydrogen–deuterium exchange of olefin. Product dependence on pressure		*8*, *20*, *82*, 9
9 $H + C_3H_6 \rightarrow n\text{-}\dot{C}_3H_7^*$ $\rightarrow iso\text{-}\underset{\cdot}{C}_3H_7^*$	35	d.u.d. Prod. depend. on press	$\rightarrow \cdot CH_3 + C_2H_4$	*85*, *9b*, 10
10 $H + C_4H_8\text{-}2 \rightarrow \underset{\cdot}{C}_4H_9^*$	37–38	d.u.d. *cis-trans*-Isomerisation of but-2-ene. Prod. depend. on press.	$\rightarrow \cdot CH_3 + C_3H_6$ $\rightarrow CH_3CH_2 + C_2H_4$	*19*, *94*
$+ C_4H_8\text{-}1 \rightarrow \underset{\cdot}{C}_4H_9^*$	39			
11 $O + SO \rightarrow SO_2\dagger$	115	Emission (continuum in the visible)		11

[7] (*a*) E. Gorin, W. Kauzman, J. Walter, and H. Eyring, *J. Chem. Phys.*, 1939, 7, 633; (*b*) B. deB. Darwent and E. W. R. Steacie, *ibid.*, 1948, **16**, 381.

[8] C. A. Heller and A. S. Gordon, *J. Phys. Chem.*, 1960, **64**, 390.

[9] (*a*) S. Toby and H. I. Schiff, *Canad. J. Chem.*, 1956, **34**, 1061; (*b*) P. J. Boddy and J. C. Robb, *Proc. Roy.Soc.*, 1959, **249**, *A*, 518; A. H. Turner and R. J. Cvetanović, *J. Chem. Phys.*, 1959, **37**, 1075; K. R. Jennings and R. J. Cvetanović, *ibid.*, 1961, **35**, 1233; J. H. Current and B. S. Rabinovitch, *ibid.*, 1963, **38**, 783, 1967.

[10] W. J. Moore, *J. Chem. Phys.*, 1948, **16**, 916; M. D. Scheer and R. Klein, *J. Phys. Chem.*, 1961, **65**, 375; W. E. Falconer, B. S. Rabinovitch, and R. J. Cvetanović, *J. Chem. Phys.*, 1963, **39**, 40.

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TABLE B.—*continued*

Reactions§	$-\Delta H^{\#}$ (kcal./mole)	Evidence for chemical activation	Reactions of activated molecule (other than deactivation or reverse reaction)	Refs.
12 $O + NO \rightarrow NO_2\dagger$ (C state)	71	Emission ("air afterglow"): $NO_2\dagger(C) \rightarrow NO_2\dagger(B)$ $NO_2\dagger \rightarrow NO_2 + h\nu$		*37a*, 12
13 $O + NO_2 \rightarrow NO_3^*$	50	d.u.d. Isotopic exchange		13
14 $O + O_2 \rightarrow O_3^*$	24	d.u.d.		*37*, *46a* 12*b*
15 $O + CO \rightarrow CO_2\dagger$(triplet) $\rightarrow CO_2^*$ (singlet)	127	d.u.d. Emission in visible. $CO_2\dagger$(triplet) $\rightarrow CO_2\dagger$(singlet) $CO_2\dagger$(singlet) $\rightarrow CO_2 + h\nu$		*53*, *54*, *73*
16 $O(1D) + CO_2 \rightarrow CO_3^*$		d.u.d. Isotopic exchange		14
17 O + ethylene propylene butenes pent-2-ene butadiene other olefins $\rightarrow$intermediate†	80—90	d.u.d. Prod. depend. on press	→ epoxide → carbonyl compound → other rearrangement or fragmentation	*57a*, 15
18 $O(^1D) + C_4H_8 \rightarrow$ epoxide*	~130	Prod. depend on press.	→ carbonyl compound → fragmentation products	*57b*

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[12] (*a*) H. P. Broida, H. I. Schiff, and T. M. Sugden, *Trans. Faraday Soc.*, 1961, **57**, 259; (*b*) D. Garvin, P. P. Gwyn, and J. W. Moskowitz, *Canad. J. Chem.*, 1960, **38**, 1795.

[13] F. E. Blacet, T. C. Hall, and P. A. Leighton, *J. Amer. Chem. Soc.*, 1962, **84**, 4011; M. A. A. Clyne and B. A. Thrush, *Trans. Faraday Soc.*, 1962, **58**, 511; *J. Chem. Phys.*, 1963, **38**, 1252; S. W. Benson, *ibid.*, 1963, **38**, 1251.

[14] R. J. Cvetanović, *Chem. in Canada*, 1963, **15**, No. 4, 56.

[15] R. J. Cvetanović, *J. Chem. Phys.*, 1956, **25**, 376; 1960, **33**, 1063; *Canad. J. Chem.*, 1955, **33**, 1684; 1958, **36**, 623; S. Sato and R. J. Cvetanović, *ibid.*, 1958, **36**, 279, 970; 1959, **37**, 953; R. J. Cvetanović and L. C. Doyle, *ibid.*, 1960, **38**, 2187.

TABLE B.—*continued*

	Reactions§	$-\Delta H^{\#}$ (kcal./mole)	Evidence for chemical activation	Reactions of activated molecule (other than deactivation or reverse reaction)	Refs.
19	N + ethylene acetylene propylene butenes $\} \rightarrow$ intermediate*		Prod. depend. on press.	→ decomposition products	16
20	X + olefin → Xolefin* X = F, Cl, Br, I olefin = dihalogeno-olefin or but-2-ene	~44(F) ~18(Cl) ~ 5(Br) ~−9(I)	Olefin isomerised or exchanged		*14*, *15*, 17
21	$Cl + O_2 \rightarrow ClO_2$*	~8	d.u.d. Cl catalysed isotopic scrambling in O_2. O_2 catalysed recomb. of Cl atoms		18
22	RS· + but-2-ene → $RS\dot{C}_4H_8$*	~15(?)	Olefin isomerised		19
23	RR′P· + but-2-ene → $RR'P\dot{C}_4H_8$*		Olefin isomerised		20

[16] (*a*) H. G. V. Evans, G. R. Freeman and C. A. Winkler, *Canad. J. Chem.*, 1956, **34**, 1271; (*b*) W. G. Zinman, *J. Phys. Chem.*, 1960, **64**, 1343; J. T. Herron, *J. Chem. Phys.*, 1960, **33**, 1273.

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[18] R. A. Ogg, jun., *J. Chem. Phys.*, 1953, **21**, 2078; S. W. Benson and J. H. Buss, *ibid.*, 1957, **27**, 1382.

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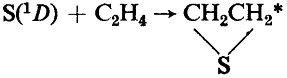
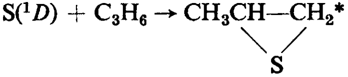
TABLE B.—*continued*

Reactions§	$-\Delta H^{\#}$ (kcal./mole)	Evidence for chemical activation	Reactions of activated molecule (other than deactivation or reverse reaction)	Refs.
24 $R\cdot + \text{olefin} \rightarrow \text{radical}^*$ $R\cdot = \cdot CH_3, \cdot CD_3, \cdot CF_3$	25	Proposed intermediate in displacement or olefin isomerisation reaction	$\rightarrow \text{olefin}' + R'$ $R' = \cdot CD_3, \cdot CH_3, CH_3CO, Cl$	*26*, 17*b*, 21*a*
24*a* $R\cdot + \text{acetylene} \rightarrow \text{radical}^*$ $R\cdot = \text{i-propyl or t-butyl}$	30	Proposed intermediate	→ possible rearrangement	21*b*
25 $NO + C_2H_2D_2 \rightarrow NO{\cdot}C_2H_2D_2^*$	−27	Olefin isomerised		*21*
26  $S(^1D) + C_2H_4 \rightarrow CH_2CH_2^*$	73	Kinetic characteristics		22
 $S(^1D) + C_3H_6 \rightarrow CH_3CH{-}CH_2^*$				
$S(^1D) + \text{alkanes} \rightarrow \text{mercaptans}^*$		d.u.d. Prod. depend. on press.		
27 $:CH_2 + CH_2{:}CH_2 \rightarrow \text{cyclopropane}^*$	~85	d.u.d. Prod. depend. on press.	$\rightarrow CH_3CH{=}CH_2$ → geometrical isomer	23*a*, *32, 101a*
27*a* $:CH_2 + C_2H_xF_{4-x} \rightarrow \text{fluorocyclopropane}^*$		d.u.d.	→ fluoropropylenes	*23b*

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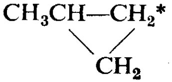
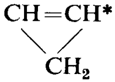
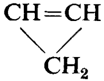
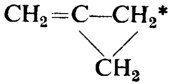
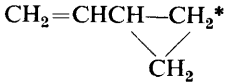
[21] (*a*) J. N. Pitts, R. S. Tolberg, and T. W. Martin, *J. Amer. Chem. Soc.*, 1954, **76**, 2843; R. E. Varnerin, *ibid.*, 1955, **77**, 1426; J. R. McNesby and A. S. Gordon, *ibid.*, 1957, **79**, 5902; P. Kebarle and W. A. Bryce, *Canad. J. Chem.*, 1957, **35**, 576; J. N. Pitts, jun., D. D. Thompson, and R. W. Woolfolk, *J. Amer. Chem. Soc.*, 1958, **80**, 66; J. H. Binks, J. Gresser, and M. Szwarc, *J.*, 1960, 3944; (*b*) J. A. Garcia Dominguez and A. F. Trotman-Dickenson, *J.*, 1962, 940.

[22] O. P. Strausz and H. E. Gunning, *J. Amer. Chem. Soc.*, 1962, **84**, 4080; *Chem. in Canada*, 1963, **15**, No. 4, 58.

[23] (*a*) H. M. Frey, *J. Amer. Chem. Soc.*, 1957, **79**, 1259; B. S. Rabinovitch, E. Tschiukow-Roux, and E. W. Schlag, *ibid.*, 1959, **81**, 1081; (*b*) B. A. Grzybowska, J. H. Knox, and A. F. Trotman-Dickenson, *J.*, 1963, 746.

TABLE B.—*continued*

	Reactions§	$-\Delta H^{\#}$ (kcal./mole)	Evidence for chemical activation	Reactions of activated molecule (other than deactivation or reverse reaction)	Refs.
28	:CH$_2$ + CH$_3$CH=CH$_2$ → 	~85	d.u.d. Prod. depend. on press.	→ all isomeric butenes	*100*, 24
29	:CH$_2$ + but-2-ene → dimethyl▽* + isobutene↗	~85	d.u.d. Prod. depend. on press.	→ structural isomers → geometrical isomer	*18*, *32*, 25
30	:CH$_2$ + CH≡CH → 		By analogy (no  isolated)	→ CH$_2$=C=CH$_2$ → CH$_3$C≡CH	26
31	:CH$_2$ + CH$_2$=C=CH$_2$ →  → CH$_3$CH=C=CH$_2$*		Prod. depend. on press.	CH≡CH + C$_2$H$_4$ structural isomers structural isomers	27
32	:CH$_2$ + CH$_2$=CHCH=CH$_2$ → 		Prod. depend. on press.	→ pentadienes cyclopentene*	28

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[24] J. H. Knox and A. F. Trotman-Dickenson, *Chem. and Ind.*, 1957, 1039.

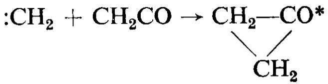
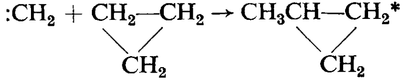
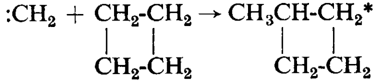
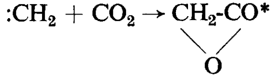
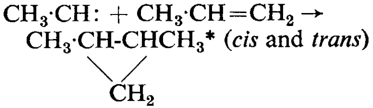
[25] H. M. Frey, *J. Amer. Chem. Soc.*, 1958, **80**, 5005; *Proc. Roy. Soc.*, 1959, *A*, **250**, 409; J. H. Knox and A. F. Trotman-Dickenson, *J.*, 1958, 2897.

[26] H. M. Frey, *Chem. and Ind.*, 1960, 1266.

[27] H. M. Frey, *Trans. Faraday Soc.*, 1961, **57**, 951.

[28] H. M. Frey, *Trans. Faraday Soc.*, 1962, **58**, 516; B. Grzybowska, J. H. Knox, and A. F. Trotman-Dickenson, *J.*, 1962, 3826.

TABLE B.—*continued*

	Reactions§	$-\Delta H^{\#}$ (kcal./mole)	Evidence for chemical activation	Reactions of activated molecule (other than deactivation or reverse reaction)	Refs.
33			Proposed intermediate	$\rightarrow C_2H_4 + CO$	29
34	$:CH_2 + H_2 \rightarrow CH_4^*$	103	Proposed mechanism	$\rightarrow \cdot CH_3 + H$	*40*, 30
35	$:CH_2 + CH_4 \rightarrow C_2H_6^*$	87	Proposed mechanism	$\rightarrow 2\cdot CH_3$	*40*, 31
36		91	Prod. depend. on press.	→ all isomeric butenes	*100*, *101a,b*, 24
37		~91	Prod. depend. on press.	$\rightarrow C_2H_4 + C_3H_6$	32
38	$:CH_2 + CO \rightarrow CH_2CO^*$	72	Proposed mechanism		33
39			Proposed mechanism	$\rightarrow CO + HCHO$	34
40			Assumed by analogy		35

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[29] D. A. Semenow, E. F. Cox, and J. D. Roberts, *J. Amer. Chem. Soc.*, 1956, **78**, 3221; G. B. Kistiakowsky and K. Sauer, *ibid.*, 1956, **78**, 5699; G. B. Kistiakowsky and P. H. Kydd, *ibid.*, 1957, **79**, 4825; W. B. DeMore, H. O. Pritchard, and N. Davidson, *ibid.*, 1959, **81**, 5874.

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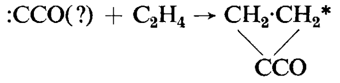
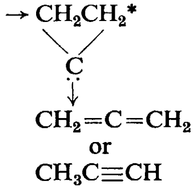
[32] H. M. Frey, *Trans. Faraday Soc.*, 1960, **56**, 1201.

[33] G. B. Kistiakowsky and W. L. Marshall, *J. Amer. Chem. Soc.*, 1952, **74**, 88; T. B. Wilson and G. B. Kistiakowsky, *ibid.*, 1958, **80**, 2934.

[34] G. B. Kistiakowsky and K. Sauer, *J. Amer. Chem. Soc.*, 1958, **80**, 1066.

[35] H. M. Frey, *Chem. and Ind.*, 1962, 218; *J.*, 1962, 2293.

TABLE B.—*continued*

	Reactions§	$-\Delta H^{\#}$ (kcal./mole)	Evidence for chemical activation	Reactions of activated molecule (other than deactivation or reverse reaction)	Refs.
41	 $:CCO(?) + C_2H_4 \rightarrow CH_2{\cdot}CH_2^*$ (CCO)		Proposed mechanism	 $\rightarrow CH_2CH_2^*$ (C:) $\downarrow$ $CH_2{=}C{=}CH_2$ or $CH_3C{\equiv}CH$	36
42	$\cdot CH_3 + \cdot CH_3 \rightarrow C_2H_6^*$	83	Observed pressure dependence		1*a*, 37
43	$\cdot CH_3 + NO \rightarrow CH_3{\cdot}NO^*$	~51	d.u.d.		1*a*, 38
44	$\cdot CH_3 + O_2 \rightarrow CH_3O_2^*$	~5	d.u.d.	$\rightarrow HCHO + OH$	1*a*, 38*a*, 39
45	$\cdot CH_3 + (CF_3)_2CO \rightarrow (CF_3)_2CO{\cdot}CH_3^*$		Proposed intermediate in displacement reaction	$\rightarrow CF_3COCH_3 + \cdot CF_3$	40
46	$R\cdot + NO_2 \rightarrow RNO_2^*$ $\rightarrow RONO^*$ $R\cdot \equiv (C_1\text{-}C_4)$	~57 ~57	d.u.d. d.u.d.	 $\rightarrow R\dot{O} + NO$	*42*

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[36] K. Bayes, *J. Amer. Chem. Soc.*, 1962, **83**, 3712; 1962, **84**, 4077; R. T. Mullen and A. P. Wolf, *ibid.*, 1962, **84**, 3214.

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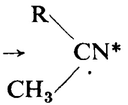
TABLE B.—*continued*

	Reactions§	$-\Delta H^{\#}$ (kcal./mole)	Evidence for chemical activation	Reactions of activated molecule (other than deactivation or reverse reaction)	Refs.
47	$\mathrm{R\cdot + CH_3CN \rightarrow}$  $\mathrm{R(CH_3)\dot{C}N^*}$		Proposed intermediate	$\rightarrow \mathrm{\cdot CH_3 + RCN}$	40*b*, 41
	$(\mathrm{R\cdot = H, \cdot CN, \cdot CH_3, \cdot CF_3})$				
48	$\mathrm{F + NO \rightarrow NOF^*}$	55	Emission in visible		42
49	$\mathrm{NH_3 + BF_3 \rightarrow NH_3BF_3^*}$	28	d.u.d.		*41*, 43
	$\mathrm{R_3N + BF_3 \rightarrow R_3NBF_3^*}$	~28	d.u.d.		
50	$\mathrm{NO_2 + NO_2 \rightarrow N_2O_4^*}$	13	d.u.d.		*79*, 44
51	$\mathrm{NO_2 + NO_3 \rightarrow N_2O_5^*}$	21	d.u.d.		45
52	$\mathrm{\cdot NF_2 + \cdot NF_2 \rightarrow N_2F_4^*}$	19	d.u.d.		*17*
53	$\mathrm{X + X \rightarrow X_2^*}$		d.u.d. Continuous emission		*81*
	X = atom				
	e.g., $\mathrm{Br(^2\mathit{P}_3/_2) + Br(^2\mathit{P}_1/_2) \rightarrow Br_2(^3\mathit{\Pi}_{0+u})}$				

† Electronic excitation occurs as well as vibrational excitation.

* Vibrational excitation only.

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TABLE C. *Bimolecular exchange reactions.*

Reaction§	$-\Delta H$ (kcal. /mole)	Electronic state of excited product	Level of vibrational excitation#	Detection of Activation	Refs.
1 $H + O_3 \rightarrow OH^* + O_2$	80	G (ground state)	$v \leqslant 9$ (75 kcal.)	I.r. emission	*87*
2 $H + O_3 \rightarrow OH^* + O_2\dagger$	42	$^1\Sigma_g^+$	$v = 4$ (35·5 kcal.)	Emission from $^1\Sigma_g^+$ Higher proportion of OH* formation in v = 4 state	*87c, e*
3 $H + HO_2 \rightarrow OH^* + OH$	38	G	$v \leqslant 3$ (27·6 kcal.)	I.r. emission	46
4 $H + NO_2 \rightarrow OH^* + NO$	31	G	$v \leqslant 1$		*44*
5 $H + N_2H \rightarrow NH\dagger + NH$		$^1\Pi$		Emission, $^1\Pi \rightarrow {}^1\Delta$	*33*
6 $H + Cl_2 \rightarrow HCl^* + Cl$	45	G	$v \leqslant 5$ (36·8 kcal.)	I.r. emission	*13, 88*
$D + Cl_2 \rightarrow DCl^* + Cl$	47	G	$v \leqslant 5$	I.r. emission	*88b*
7 $H + Br_2 \rightarrow HBr^* + Br$	41	G	$v \leqslant 6$	I.r. emission	47
8 $H + NOCl \rightarrow HCl^* + NO$	65	G	$v \leqslant (10?)$ (63·6 kcal.)	I.r. emission	*88b, 91*
9 $H + F_2 \rightarrow HF^* + F$	98	G	$v \leqslant 9$ (86 kcal.)	I.r. emission	48

§ Reactant atoms are in ground electronic state unless otherwise indicated.
# Values in parentheses refer to the highest value of v cited.

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TABLE C.—*continued*

Reaction§	$-\Delta H$ (kcal. /mole)	Electronic state of excited product	Level of vibrational excitation#	Detection of Activation	Refs.
10 $O + NO_2 \rightarrow O_2^* + NO$	46	G	$v \leqslant 8$ (34 kcal.) $v \leqslant 12$ (49 kcal.)	U.v. absorption; non-Boltzmann distribution, $v = 1$, mainly U.v. absorption	*90a* *90b* *43a*
11 $O + ClO_2 \rightarrow O_2^* + ClO$	61	G	$v \leqslant 8$ (34 kcal.)	U.v. absorption	*90*
12 $O + O_3 \rightarrow O_2^* + O_2$	93	G	$v \leqslant 17$ (19) (66·5 kcal.)	U.v. absorption	*43*, *46b*, 49
13 $O(^1D) + O_3 \rightarrow O_2^* + O_2$	138	G	$v \leqslant 18, 19$	I.r. emission O_2^* can promote decomposition of O_3	*43a*, *46*, 49a
14 $O(^1D) + H_2 \rightarrow OH^* + H$ $O(^1D) + H_2O \rightarrow OH^* + OH$ $O(^1D) + HCl \rightarrow OH^* + Cl$ $O(^1D) + NH_3 \rightarrow OH^* + \cdot NH_2$ $O(^1D) + CH_4 \rightarrow OH^* + \cdot CH_3$	43 29 44 45 45	G	$v \leqslant 2$ (19·8 kcal).	I.r. emission	*43b*
15 $C_2H + O_2 \rightarrow CH\dagger + CO_2$ or $C_2H + O(^3P) \rightarrow CH\dagger + CO$	75 or 67	$A^2\Delta$ $B^2\Sigma$		Possible reactions for production of CH* from which emission occurs in acetylene flames	50
16 $CH^* + O(^3P) \rightarrow CO\dagger + H$		$A^1\Pi$		$CO(A^1\Pi) \rightarrow CO(X^1\Sigma) + h\nu$ (vacuum u.v. emission)	50

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TABLE C.—*continued*

	Reaction§	$-\Delta H$ (kcal. /mole)	Electronic state of excited product	Level of vibrational excitation#	Detection of Activation	Refs.
17	$N + NO \rightarrow N_2^* + O$	75	G	>24 kcal.	$N_2^* + O_3 \rightarrow N_2 + O_2 + O$	*45*
18	$N + NC_2H_4 \rightarrow C_2H_4^* + N_2$				Suggested reaction	16*a*, 51
19	$Br + O_3 \rightarrow BrO^* + O_2$	19 $[Br(^2P_{3/2})]$	G	$v \leqslant 4$ (8 kcal.)	Absorption spectra	52
		29·5 $[Br(^2P_{1/2})]$				
20	$Cl + O_3 \rightarrow ClO^* + O_2$	40 $[Cl(^2P_{3/2})]$	G	$v \leqslant 5$ (?) (11 kcal.)		
		42·5 $[Cl(^2P_{1/2})]$	G			
21	$S + S_2Cl_2 \rightarrow S_2^* + SCl_2$	51	G	$v = 5 - 12$ (25 kcal.)	Absorption spectra $^3\Sigma_g^- \rightarrow 3\Sigma_u^-$	53
22	$X + Na_2 \rightarrow NaX^* + Na$	Cl 81 Br 71 I 54	G	At least 48·5 kcal.	Sodium D line emission	*9*, *70*, *71*
23	$Na + ClX \rightarrow NaX^* + Cl$	Cl 52 Br 39? I 53?				
24	$Na + HgX \rightarrow NaX^* + Hg$	Cl 75 Br 71?				

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TABLE C.—*continued*

	Reaction§	$-\Delta H$ (kcal. /mole)	Electronic state of excited product	Level of vibrational excitation#	Detection of Activation	Refs.
25	$RX + Na \rightarrow R + NaX^*$ (R = olefin or cyclic compound)		G	At least 48·5 kcal.	Sodium D line emission	*72*
26	$NO + O_3 \rightarrow NO_2^* + O_2$	49	High vibrational electronic ground state or metastable electronic state		Emission (5900—10,850 Å)	54
27	$C(^3P) + CH(^2\Pi) \rightarrow C_2\dagger + H(^2S)$	61	$A^3\Pi_g$	$v \leqslant 2$	Swan emission band	55
	$C(^3P) + CCl(^2\Pi) \rightarrow C_2\dagger + Cl$		$A^3\Pi_g$	$v \leqslant 8$ $v = 7,8$ preferentially excited		
28	$CH_3CH + CH_3CHN_2 \rightarrow$ *trans*-$C_4H_8^* + N_2$				Isomerisation to *cis*-$C_4H_8^*$ unless deactivated	35
29	$CH_3 + O_2 \rightarrow CH_2O + OH$	43	G		Proposed reaction cf. Table B. reaction 44	39*b*

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TABLE D. *Termolecular reactions.*‡

	Reaction	Evidence for chemical activation	Refs.
1	$H + H + M \rightarrow H_2 + M$	Third body requirement	56
2	$H + H + Na \rightarrow H_2 + Na\dagger$	Na D-line emission	*2b*, 57
3	$H + H + Tl(\text{or } Pb) \rightarrow H_2 + Tl\dagger$ (or $Pb\dagger$)	Emission from Tl $(^2S_{1/2})$ [or $Pb(^3P_1)$]	*53*
4	$H + H + S_2 \rightarrow H_2 + S_2\dagger$	Emission from $S_2\dagger$	58
5	$N + N + M \rightarrow N_2 + M$	Third body requirement	*75*, *76*
6	$N + N + O \rightarrow N_2 + O(^1S)$	Emission from $O(^1S)$	59
7	$N + N + TlX \rightarrow N_2 + X + Tl\dagger$ (X = F, Cl, Br, I)	Emission from $Tl\dagger$	60
8	$O + O + M \rightarrow O_2 + M$	Third body requirement	*52d*, 61
9	$Br + Br + M \rightarrow Br_2 + M$	Third body requirement	*51*,*52b*,62
10	$I + I + M \rightarrow I_2 + M$	Third body requirement	*51*, *52a–c*
11	$H + Cl + M \rightarrow HCl^* + M$	Emission from HCl^*	*88b*
12	$H + Cl + Tl (\text{or} Pb) \rightarrow HCl + Tl\dagger$ (or$Pb\dagger$)	Emission from $Tl\dagger$ (or $Pb\dagger$)	*55*
13	$H + Br + M \rightarrow HBr^* + M$	Emission from HBr^*	47
14	$H + Br + Tl \rightarrow HBr + Tl\dagger$	Emission from $Tl\dagger$	*55*
15	$N + O + M \rightarrow NO\dagger + M$	Emission from $NO\dagger$	63
16	$N + Br + M \rightarrow NBr\dagger + M$	Emission from $NBr\dagger$	64

‡ (Reactions given are not intended to represent the mechanism, necessarily.)

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