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Abstract

Full Text

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On the Additivity of Free Energies of Activation of Gas-Phase Free-Radical Reactions

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The most essential generalizations of the regularities determining the influence of the structure of compounds on their reactivity in free-radical gas-phase reactions are Polanyi' s rule and the relation of N. N. Semenov based on it ([1,2]). In recent years a number of empirical formulas have been proposed that relate the activation energies of reactions of two radicals with the same molecules ([3,6]). As can be shown, in principle these formulas can be obtained using Semenov' s relation. Analysis of a large body of experimental data on rate constants of free-radical gas-phase reactions has led us to the conclusion that the free energies of activation of these reactions may be regarded as additive quantities consisting of two independent increments—molecular and free-radical. This makes it possible, using a set of increments, to find in a simple way the rate constants for any pair "free radical—molecule."

In Fig. 1 are presented the values of the free energies of activation of reactions of the type $\dot{R}\cdot + R'H \rightarrow RH + R'\cdot$ for the radicals $CH_3\cdot$ and $CF_3\cdot$ with a series of different compounds at 436°K, calculated from the data of works ([7–13]) (for the standard concentration here and everywhere below, the mole per 1 cm^3 is adopted). It is clearly seen that the difference $\Delta F_h^{\#} - \Delta F_f^{\#} = \text{const}$ (the subscript h refers to the radical $CH_3\cdot$; f to $CF_3\cdot$). From this it may be assumed that the share of the free energy contributed to the activated complex by each free radical is the same and does not depend on the nature of the reacting molecule. Let us take, conventionally, this share for the methyl radical to be $\Delta F_h^r = 10$ kcal. Then the share of the molecule will be $\Delta F^m = \Sigma F_h^{\#} - 10$ kcal. Let us further suppose that the molecular share of the free energy of activation, in turn, does not depend on the nature of the reacting radical. In other words, to each molecule and to each free radical we assign a definite increment of the free energy of activation, on the basis of which the total free energy of activation for the reaction of any molecule—radical pair can be obtained by summing these quantities: $\Delta F^{\#} = \Delta F^m + \Delta F^r$.

Fig. 1. Comparison of the free energies of activation for reactions of $CH_3\cdot$ (*I*) and $CF_3\cdot$ (*II*). Abscissa axis:
1—CH_4;
2—C_2H_6;

Fig. 2

Figure 1: Fig. 2

3–neo-C_5H_{12};
4–*n*-C_4H_{10};
5–iso-C_4H_{10};
6–$(CH_3)_2CH$—$CH(CH_3)_2$;
7–cyclo-C_6H_{12};
8–$C_6H_5CH_3$;
9–cyclo-C_5H_{10};
10–C_6H_6.

If these assumptions are valid, then the experimental points for the trifluoromethyl radical in the coordinates $\Delta F_f^{\ddagger}$ and $\Delta F^m = \Delta F_h^{\ddagger} - 10$ should give a straight line with unit slope. As can be seen from Fig. 2, this is indeed the case. For the trifluoromethyl radical we obtain $\Delta F_f^r = 6.2$ kcal (the share of the free energy contributed to the activated complex). The difference $\Delta\Delta F^r = \Delta F_f^r - \Delta F_h^r = -3.8$ kcal serves as a measure of the reactivity of trifluoromethyl radicals relative to methyl radicals. This corresponds to the fact that the former radical is approximately 100 times more reactive than the latter.

Fig. 2. Dependence between the free energy of activation of the reaction of $CH_3\cdot$ (*I*) and $CF_3\cdot$ (*II*) and the molecular increments of the free energy of activation (ΔF^m).
1 –CH_4; 2 –C_2H_6; 3 –*neo*-C_5H_{12}; 4 –C_6H_6; 5 –$C_8H_5CH_3$; 6 –C_3H_8; 7 –cyclo-C_6H_{12}; 8 –cyclo-C_5H_{10}; 9 –$(CH_3)_2CH - CH(CH_3)_2$; 10 –*n*-C_4H_{10}; 11 –iso-C_4H_{10}.

The reactivity of various molecules is characterized by the increment $\Delta F^m = \Delta F_i^{\ddagger} - \Delta F_i^r$. To determine these increments with good accuracy, it is necessary to have information on as large a number as possible of reactions of different radicals with the same molecules. Then

$$\Delta F^m = \frac{\sum_1^n \left(\Delta F_i^{\ddagger} - \Delta F_i^r\right)}{n}.$$

At present this averaging can be carried out using data for only two radicals: methyl and trifluoromethyl. The values obtained in this way are given in Table 1 (437° K).

In Fig. 3 the values of the free energies of activation are presented as functions of the corrected values of the molecular increments of the free energy. Points for the ethyl, perfluoro-*n*-propyl, and methoxyl radicals are also plotted in the same figure ([14–18]). Despite the limited number of these points and the considerable scatter, it is evident that their arrangement can be approximately represented

Fig. 3

Figure 2: Fig. 3

by straight lines with slope equal to 1. Table 1 gives the increments of the free energy of activation for radicals (437° K). As with free radicals, so also with molecules, a higher value of the increment corresponds to a lower reactivity.

From the standpoint of activated-complex theory, the division of the free energy of activation into increments means division into increments of the heat and entropy of activation. Hence for the activation energies of the reactions of $CH_3\cdot$ and $CF_3\cdot$ we have:

$$E_h = E^m + E_h^r,$$

$$E_f = E^m + E_f^r,$$

where E^m and E^r are the molecular and radical increments of the activation energy.

Fig. 3. Same as in Fig. 2, with refined values of the molecular increments.

Subtracting one equation from the other, we obtain:

$$E_h - E_f = E_h' - E_f' = \text{const.} \tag{1}$$

Table 1 gives the differences in activation energies (ΔE_{hf}) for the reactions of various compounds with the radicals $CH_3\cdot$ and $CF_3\cdot$. Within the limits of error of determination, an approximate constancy of the differences in activation energies is indeed observed (3.1 ± 0.5 kcal)

Table 1

Radical	$\Delta F_f'$, kcal	Compound	ΔF^m, kcal	ΔF_{hf}, kcal
$C_2H_5\cdot$	12.0	CH_4	7.05	4.0
$CH_3\cdot$	10.0	C_2H_6	4.2	3.5
n-$C_3F_2\cdot$	7.2	C_6H_6	4.0	2.9
$CF_3\cdot$	6.2	$(CH_3)_4C$	3.8	2.4
$CH_3O\cdot$	5.2	C_3H_8	2.9	–
		$C_6H_5CH_3$	2.7	2.6
		n-C_4H_{10}	2.45	3.1
		$(CH_3)_3CCH$	2.05	2.9
		cyclo-C_6H_{12}	1.9	3.3

Radical	$\Delta F'_f$, kcal	Compound	ΔF^m, kcal	ΔF_{hf}, kcal
		cyclo-C_5H_{10}	1.6	3.6
		$(CH_3)_2CH{-}CH(CH_3)_2$	0.8	6.1

of activation energies, except for the case of 2,3-dimethylbutane, which is apparently connected with an incorrect value of the activation energy for its reaction with $CF_3\cdot$ (1.7 kcal). If relation (1) is not obeyed for a series of compounds, then reactions with them cannot be included in the general system of increments. This is the case for acetone, deuterium, hydrogen, and also HD. Data on the reactions of these substances are contained in papers ([5,9,11]).

For activation entropies, the experimental data have very low accuracy. For the reactions under consideration they are presented in Fig. 4. As can be seen, line II ($CF_3\cdot$) in general repeats the course of line I ($CH_3\cdot$), although individual points violate this tendency ([3,6,10]). One of these points, giving the sharpest deviation, relates to the reaction of $CF_3\cdot$ with 2,3-dimethylbutane, the data for which, as indicated above, are doubtful. Experimental errors are in all probability also connected with the deviations in the case of points 3 and 10. Taking into account the generally low accuracy of determining preexponential factors, one may apparently consider that the difference in activation entropies in the reactions of different radicals with the same molecules is approximately constant. Just as in the case of activation heat, this makes it possible to regard the activation entropy as an additive quantity. A similar point of view is held by Trotman-Dickenson ([5]).

Fig. 4. Comparison of activation entropies for the reactions of $CH_3\cdot$ (I) and $CF_3\cdot$ (II). The numbering is the same as in Fig. 1.

The consideration carried out shows that the rates of gas-phase reactions of free-radical substitution can be readily obtained if the corresponding increments are known. This opens a very effective route for systematizing data on the kinetics of elementary gas-phase reactions of free-radical substitution, and also for obtaining information on the reactivity of compounds and radicals for which experimental data are available in insufficient quantity or

are absent. It must be borne in mind that the free energies of activation depend on temperature. Therefore, to obtain complete information on reaction rates, data on the temperature dependence of the increments are necessary. This presents no difficulty, since the Arrhenius parameters of the reactions, with the aid of which the increments for a temperature of 473° K were obtained in the present work, are known and make it possible to find these increments for other temperatures in an analogous manner.

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Note: Figure translations are in progress. See original paper for figures.