THE PREEXPONENTIAL FACTOR OF REACTIONS OF RADICAL DECOMPOSITION OF NITRO COMPOUNDS

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A large number of experimental data on the thermal decomposition of aliphatic nitro and α-halonitro compounds in the gas phase are known. There are approximately 30 compounds, for which a monomolecular mechanism of decomposition by dissociation of the $C-N$ bond (radical decomposition) has been strictly demonstrated

$$RNO_2 \rightarrow R + NO_2 \tag{1}$$

and the kinetic characteristics of this elementary step have been determined (Table 1). Interesting peculiarities of these reactions are the high values of the preexponential factor A, which vary substantially $(10^{14.3}-10^7 \sec^{-1})$ within the framework of one reaction series. In this work an attempt was made to discuss the dependence of A on the structure of nitro compounds in greater detail than before [12, 13] and to qualitatively explain this dependence on the basis of general theoretical concepts of the reactions of decomposition of a molecule into two radicals.

Most of the data cited in Table 1 were obtained by a manometric method under static conditions. The maximum error in the determination of the activation energy E under these conditions is estimated at 1.0-2 kcal/mole, which corresponds to a change in log A by 0.5-1 unit. The real error for many compounds evidently does not exceed 1 kcal/mole. This is evidenced, for example, by the good agreement of the activation energies for structurally close substances (see Table 1, 11-12; 13-14; 15-17; 20-22). In the case of polynitro- and halonitroalkanes, objective factors promoting the reliable determination of E are the comparatively low (and, consequently, well regulatable) temperatures of decomposition 100-200°, the absence of chain processes, and the insensitivity of the decomposition process to impurities.

For two substances — nitroform and fluorodinitromethane — an influence of the surface of the vessel on the rate of decomposition has been observed [8]. A consideration of the heterogeneous reaction was performed most carefully for nitroform; the data for fluorodinitromethane are less reliable. Apparently the value of E is overestimated in the case of $FC(NO_2)_2CF(NO_2)_2$ [9]. For all compounds except for nitromethane, the influence of the reversibility of step (1) on the kinetic parameters of decomposition was not studied specially. The available data on chlorotrinitromethane [4] show that, at least for polynitroalkanes, the role of reversibility is minor. A substantial influence of the surface, secondary reactions, back recombination, and the total pressure is observed in the case of nitromethane. However, all the complicating factors have been sufficiently reliably considered for this compound [1].

In [5, 6, 9, 10, 12, 13] the following empirical rules, pertaining to the influence of the structure on the activation energy of the radical decomposition of polynitro compounds, were noted: 1) in the series $RCH_n \cdot (NO_2)_{3-n}$, E does not depend on the length of the alkyl radical R. For n = 1, E = 47-48 kcal/mole; for n = 0, E = 41-43 kcal/mole; 2) substituents R, H, and F in the α-position to the nitro group have the same influence on the activation energy; 3) when one NO_2 group is replaced by Cl, the activation energy is reduced by approximately 1 kcal/mole; 4) atoms of Br and I reduce E to a greater degree than Cl.

Using these rules, we can eliminate the substantial experimental errors permitted in the determination of E. In particular, the values of E and consequently A seem too high for $C_3H_9(NO_2)_3$, $HFC(NO_2)_2$, $CH_3C(NO_2)_2CH_3$, as do the data for $C(NO_2)_4$ obtained in [7]. The values of E "corrected" according to

TABLE 1

Group	No. of orders	Compound	Temperature interval, °C	E, kcal/mole	lg A (A, sec⁻¹)	lg A/σ	ΔS≠ (473°) gibbs/mole†	Literature reference
1	1	CH_3NO_2	360-390	54.3	14.34	14.34	4.17	[1]
			380-430	53.6	14.6	14.6	5.359	[2]
2	2	CCl_3NO_2	140-170	37.4	15.35	15.35	8.808	[3]
	3	$CCl_2(NO_2)_2$	110-150	34.3	15.26	14.96	7.006	[4]
	4	$CCl(NO_2)_3$	120-165	36.4	15.75	15.27	8.423	[4]
	5	$CBr(NO_2)_3$	110-160	36.2	16.10	15.52	10.024	[4]
	6	$CI(NO_2)_3$	113-150	34.4	15.25	14.77	6.137	[4]
	7	$FClC(NO_2)_2$	170-214	41.5	15.70	15.40	9.018	[5]
	8	$FBrC(NO_2)_2$	170-210	39.5	15.30	15.00	7.189	[5]
	9	$FIC(NO_2)_2$	160-197	39.7	15.70	15.40	9.018	[5]
	10	$C(NO_2)_4$	86-177	38.2	16.30	15.70	10.39	[6]
		$C(NO_2)_4$	170-223	40.9	17.53	16.93	16.016	[7]
3	11	$HC(NO_2)_3$	180-200	42.4	15.94	15.46	9.293	[8]
	12	$FC(NO_2)_3$	178-236	41.9	15.40	14.92	6.82	[9]
				(42.5)	15.68)	(15.20)	(8.09)	
	13	$HFC(NO_2)_2$	244-264	48.5	16.68	16.38	13.50	[8]
				(47.5)	(16.22)	(15.92)	(11.4)	
	14	$F_2C(NO_2)_2$	235-270	47.4	15.88	15.58	9.841	[9]
	15	$CH_3CH(NO_2)_2$	197-266	47.12	16.74	16.44	13.775	[10]
	16	$C_2H_5CH(NO_2)_2$	215-265	48.0	16.91	16.60	14.507	[10]
	17	$C_3H_7CH(NO_2)_2$	220-265	48.16	16.99	16.70	14.964	[10]
	18	$CH_3CF(NO_2)_2$	214-262	47.7	17.0	16.70	14.964	[9]
4	19	$CH_3C(NO_2)_2CH_3$	175-210	50.5	18.5	18.2	21.8	[11]
				(47.5)	(17.11)	(16.81)	(15.46)	
	20	$CH_3C(NO_2)_3$	160-210	43.2	17.18	16.70	14.964	[12]
	21	$C_2H_5C(NO_2)_3$	160-200	42.3	16.86	16.38	13.5	[12]
	22	$C_3H_7C(NO_2)_3$	160-200	43.6	17.70	17.22	17.342	[12]
				(42.5)	(17.2)	(16.72)	(15.05)	[12]
	23	$C(NO_2)_3C(NO_2)_3$	90-135	35.8	17.3	16.52	14.14	[6]
	24	$FC(NO_2)_2C(NO_2)_3$	88-140	36.5	17.3	16.60	14.51	[9]
	25	$FC(NO_2)_2C(NO_2)_2F$	107-180	42.2	18.03	17.4	18.17	[9]
	26	$CH_3CBr(NO_2)_2$	160-190	40.54	16.14	15.84	11.031	[13]
5	27	$CH_3CCl_2NO_2$	190-235	42.6	15.22	15.22	8.195	[13]
	28	$C_2H_5CCl_2NO_2$	200-258	42.67	15.15	15.15	7.875	[13]

*σ is the statistical factor of the reaction, equal to the number of equivalent NO_2 groups in the molecule.

†Calculated from the ratio $A = \sigma(ekT/h) e^{\Delta S^{\neq}/R}$.

the rules indicated above for these compounds with the corresponding changes in the preexponential factor are cited in parentheses in Table 1.

For convenience of comparison, the entropy of activation $\Delta S^{\neq}$ was calculated for all the compounds at the same temperature, considering the statistical factor of the reaction (see Table 1).

Using two characteristics — the value of $\Delta S^{\neq}$ and the structure of the molecules — and taking into consideration the possible experimental errors, all the available data can be divided into several groups, which are shown in Table 1. Before discussing the separation obtained, let us consider the question of the structure of the activated complex in the decomposition of nitro compounds and the influence of the structure of the activated complex on the value of A.

According to the statistical theories of monomolecular reactions, based on the method of the transition state, the increase in the preexponential factor in monomolecular reactions is associated with a decrease in the vibration frequencies or the appearance of free rotations in the transition of the molecule from the ground state to an activated complex.

In reactions of cleavage of a bond with the formation of two radicals, two types of activated complexes are distinguished: free and semirigid [14]. In a free activated complex, the radicals between which the bond is broken are at a substantial distance from one another, and, retaining a mutual bond, have free or almost free rotation around the three axes of inertia. The rate constant of the recombination of such radicals is close to the number of collisions and has a value no less than $10^{10.5}$ liters/mole·sec. Free activated

complexes arise in the cleavage of strong bonds between small radicals. When molecules are broken into two radicals, four free rotations appear in the free activated complex, which leads to an increase in A by several orders of magnitude. Judging by the value of the recombination constant for $CH_3 + NO_2$, equal to $10^{9.5}$ liters/mole·sec [15], the activated complex for this compound belongs to the semirigid type, in which the pendulum vibrations of the original molecule do not turn into free rotation of the fragments being separated, but only lower their frequency. A semirigid structure of the activated complex should also exist in all the remaining nitro compounds, since the dimensions of their radicals are greater than in nitromethane, and their decomposition is characterized by a lower activation energy.

In the case of cleavage of the C − N bond in $X_3C − NO_2$, the following factors can contribute to the increase in the preexponential factor: 1) With increasing C − N distance in the activated complex, the frequencies of the deformational vibrations associated with the C − N bond are reduced. One vibration of X − C − N turns into an out-of-plane vibration of the X_3C radical, formed in the activated complex. The degree of reduction of the frequency in this case can be measured with the aid of the secondary α-deuterium isotopic effect [16]. Without any great error it may be considered that in all cases the frequency is halved [16]. The frequencies of the two pendulum vibrations of $X_3C − N$ and the analogous vibrations of $C − NO_2$ are reduced and tend to turn into free rotation. In semirigid activated complexes, the pendulum vibrations may be reduced by 2-3-fold [14]. 2) The internal rotation relative to the C − N bond is liberated if it was inhibited in the ground state of the molecule. The maximum possible change in the entropy of the activated complex on account of liberation of the inhibited rotation is about three gibbs/mole, which leads to an approximately 4.5- fold increase in A. 3) The frequencies of the torsional vibrations (all the way up to free rotation) of the X groups next to the reaction center are reduced, not only on account of the removal of the NO_2 group, but also as a result of an increase in the X − C − X angle and a decrease in the repulsion between X groups. The effect of rotation of the neighboring groups had not previously been observed experimentally in clear form, although in principle it might be very great.

In the case of nitro compounds, two substituents − the alkyl group R and the nitro group − play the role of X, capable of rotation. Moreover, they are encountered in very varied structures and have different possibilities of rotation in the activated complex.

The general concepts enumerated in points 1)-3) aid in understanding the experimental data of Table 1.

In the case of nitromethane, for which the barrier to internal rotation is very small [17], and factors 2 and 3 are absent the increase in A in comparison with the "normal" value of 10^{13} sec^{-1} ($\Delta S^{\neq} = 0$) is due only to a decrease in the frequencies of the deformational vibrations.

A 2-fold decrease in the frequency of one nonsymmetrical vibration (1482, see [18]) of the four pendulum vibrations (1087, 1100, 477, 605 cm) gives an increase in the entropy of the activated complex of 4.7 gibbs/mole, which corresponds approximately to the experimental value.

The introduction of large halogen atoms (Cl, Br, I) or NO_2 groups into the nitromethane molecule in place of one or several hydrogen atoms leads to a sharp increase in the barrier to internal rotation around the C − N bond, and thus, for compounds 2-28 (see Table 1), together with the first factor, the second factor will also operate, since rotation around the breaking bond in the activated complex always becomes free. As is shown by a consideration of the structural models, the large halogen atoms effectively prevent internal rotation of the neighboring alkyl and nitro groups, both in the case of a tetrahedral and in the case of a flat structure of the fragment X_3C. Thus, in this case the contribution of the third factor becomes impossible. Actually, for compounds of the second and fifth groups, which have large halogen atoms in the α-position, the change in $\Delta S^{\neq}$ is equal to an average of 7.8-8 gibbs/mole and exceeds $\Delta S^{\neq}$ for nitromethane by 3-4 gibbs/mole. Such an increase corresponds, within the limits of the experimental error, to the maximum entropy change in the liberation of one inhibited internal rotation. As is well known, in such a transition the entropy change depends little on the value of the statistical sum of free rotation. Therefore, the change in the masses of the rotating fragments and the symmetry number of the rotation does not play a significant role. The main influence is exerted by the height of the barrier. Judging by the entropy change for compounds of the second and fifth groups, the barriers to rotation around the C − N bond in polynitro compounds exceed 10 kcal/mole.

If the substituents in nitromethane derivatives are H, F, and NO_2 instead of large halogen atoms, in principle, there may be an increase in $\Delta S^{\neq}$ on account of a decrease in the frequencies of the torsional vibrations of the NO_2 groups in the remaining radical in the activated complex. The third group of

compounds in Table 1 corresponds to structures for which this effect may be expected. Actually, $\Delta S^{\neq}$ for these compounds is an average of two gibbs/mole higher than for the corresponding structure of the second group. The most accurate data for tetranitromethane and nitroform show that, calculated per nitro group, $\Delta S^{\neq}$ is changed by approximately 1 gibbs/mole. Thus, the effect of reduction of the frequency of the torsional vibration of the nitro group, even in those cases when the neighboring substituents are only H and F, is very small (0.3 log unit). Evidently rotation of the nitro group is prevented by the double-bonded nature of the $C - N$ bond, arising in the free radical on account of the effect of conjugation.

If a H or F atom in compounds of the third group is replaced by an alkyl radical, then $\Delta S^{\neq}$ is sharply increased (fourth group of compounds). To explain this effect it is necessary to assume complete liberation of the internal rotation of the alkyl group in the activated complex. This hypothesis is confirmed by a number of independent facts. The NMR data are evidence of a strong inhibition of rotation around the $C-C$ bond in 1, 1, 1-trinitroethane [19]. When this compound is decomposed, a β-deuterium isotopic effect is observed [20], which indicates a change in the frequencies of the vibrations of the CH_3 group. However, the most convincing evidence of the role of internal rotation is the influence of the α-halogen on the value of A in polynitro derivatives of ethane and propane. In the presence of Br or Cl atoms in the α-position (see the fifth group of the Table), all the internal rotations in the activated complex cease, and the values of $\Delta S^{\neq}$ become the same as for the second group of compounds.

Let us note that the increase in $\Delta S^{\neq}$, explainable by internal rotation of the alkyl group, exceeds the change in $\Delta S^{\neq}$ (between the first and second groups) due to rotation around the $C - N$ bond. It also seems somewhat strange that the radicals $C(NO_2)_3$ and $FC(NO_2)_2$, possessing a large volume, have the same influence on the increase in A as simple alkyl radicals (see Nos. 23-25, Table 1), i.e., they can rotate freely in the activated complex. Possibly the cause of these anomalies lies in the inaccuracy of the experimental data, or, in addition to the rotation of the alkyl, other effects are also intensified here.

Thus, a qualitative consideration shows that the change in the preexponential factor in reactions of decomposition of aliphatic nitro compounds is influenced together or separately by all three theoretically expected factors. Moreover, evidently the effect of rotation of the neighboring groups has been detected sufficiently reliably for the first time.

CONCLUSIONS

An analysis of the experimental data on the decomposition of aliphatic nitro compounds reveals fine effects of the influence of the structure of the molecule on the preexponential factor of the reaction rate constant. The value of the latter depends on the contribution of three factors, manifested in the formation of the activated complex: liberation of the internal rotation relative to the dissociating $C - N$ bond, a decrease in the frequencies of the deformational vibrations associated with this bond, and rotation of the alkyl groups next to the reaction center.

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