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Stepwise Degradation of Polyfunctional Compounds

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Abstract—The formal kinetic peculiarities of the decomposition of polyfunctional compounds containing several identical reaction groups were used to determine the stepwise character of secondary reactions and to interpret their chemical mechanism. It was found that the degradation of difluoramines, azides, nitro esters, and aliphatic and aromatic nitro compounds always occurred stepwise via long-lived intermediate products. Only nitramines with closely spaced reaction centers exhibited deviations from this mechanism.

INTRODUCTION

Many organic compounds, in particular, explosives (it is always a topical problem to study the thermal decomposition reactions of these compounds) are homo- or polyfunctional compounds containing several identical functional groups. RDX (trimethylenetrinitramine), HMX (tetramethylenetetranitramine), TEN ($C(CH_2ONO_2)_4$), trinitrotoluene, picric acid, *sym*-trinitrobenzene (TNB), and glycidyl azide polymer (GAP, $[OCH_2CH(CH_2N_2)]^{n-}$) are examples. If the decomposition reaction is monitored by following the consumption of the initial substance, the unimolecular reaction rate constant k_n for a polyfunctional compound with the number n of functional groups is equal to nk_0, where the rate constant k_0 belongs to the corresponding monofunctional compound. However, if the reaction is monitored by following the formation of end products (weight loss, heat release, or gas evolution), as is usually done, the result depends on the ratio between the rates of the first step of decomposition and secondary reactions, which result in the complete degradation of the molecule and in the release of end products. If the first step is a rate-limiting step and the lifetimes of intermediate products are short, $k_n = nk_0$. It was found previously [1] that, if only one group disappears as a result of the first act of degradation and a long-lived intermediate, in which the reactivity of the remaining groups remained unchanged, is formed along with the release of an amount of end products, the reaction occurs stepwise according to the following scheme:

$$A_n \xrightarrow{nk_0} A_{n-1} + P_1,$$

$$A_{n-1} \xrightarrow{(n-1)k_0} A_{n-2} + P_2,$$

$$\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots$$

$$A_1 \longrightarrow P_n.$$

Although this scheme represents a consecutive reaction, which proceeds through long-lived intermediates, the buildup of the final products ΣP_i in this reaction occurs in accordance with a first-order equation on condition that $P_1 = P_2 = \ldots = P_n$ and $k_n = k_0$. The reason for the appearance of a first order and for the equality of the rate constants k_n and k_0 is in that the end products are released in equal portions at each of the intermediate steps (the above consecutive reaction scheme is based on this assumption). If a strong induction or resonance interaction between reaction centers takes place and a monofunctional analog is difficult to choose, polyfunctional compounds can be compared with each other. In stepwise degradation, the rate constant is independent of the number of reaction groups. In this case, changes in the rate due to induction or other effects should be taken into consideration. Thus, based on only formal-kinetic measurements, we can immediately determine from the ratio between constants k_n/k_0 how the reaction occurs: in a single step or stepwise. The data on the kinetic regime of secondary reactions thus obtained can be used for interpreting their chemical mechanism, however, the practical implementation of the conditions that form the basis of the scheme is an important problem. Undoubtedly, compounds with widely spaced reaction groups (for example, separated by four carbon atoms) will undergo stepwise degradation. The probability of single-step degradation or various deviations from the requirements of the scheme can increase as the groups approach each other. Such compounds frequently occur among explosives, and they are of particular interest for revealing the stepwise or single-step mechanism of degradation. In this work, based on an analysis of published experimental data on the decomposition of polyfunctional compounds (primarily homofunctional compounds) with closely spaced reac-

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Comparison of the rate constants of decomposition of mono- and polyfunctional compounds

No.	Compound	Medium	ΔT, °C	E, kcal/mol	$\log A$ [s^{-1}]	T_c, °C	k_{expt}, s^{-1}	Reference
1	$PhCH_2NF_2$	Liquid	110–145	26.3	8.33	130	1.2×10^{-6}	[2]
2	Ph_2CHNF_2	″	110–150	28.2	9.55	130	1.7×10^{-6}	″
3	$PhCH(NF_2)_2$	″	110–150	26.0	8.30	130	1.5×10^{-6}	″
4	$PhCH(NF_2)CN$		110–150	26.0	8.50	130	2.5×10^{-6}	″
5	$PhCH(NF_2)CH_2NF_2$	″	90–140	27.7	9.30	130	1.9×10^{-6}	″
6	$F_2NCH(CH_2)_4CHNF_2$	″	100–145	26.7	8.55	130	1.1×10^{-6}	″
7	$CH_3CH(NF_2)CH{=}CHCH_2NF_2$	″	110–145	24.0	6.88	130	0.7×10^{-6}	″
8	$-[OCH_2CH(CH_2N_3)]_n$, n = 5–20	″	180–205	39.4	14.10	120	1.6×10^{-6}	[3]
9	$CH_3CH_2CH_2N_3$	Gas	200–240	39.4	14.18	120	1.9×10^{-6}	[4]
10	HMX	″	230–250	32.0	13.2	200	6.0×10^{-5}	[5]
	″	″	205–250	37.5	14.2	200	9.0×10^{-5}	[6]
11	$(CH_3)_2NNO_2$ (DMNA)	″	180–240	40.6	14.1	200	1.8×10^{-5}	[7]
	″	″	180–240	40.8	14.1	200	2.2×10^{-5}	[8]
12	$O_2NHCH_2NHNO_2$ (MDNA)	Liquid	110–150	29.9	12.26	140	2.8×10^{-4}	[9]
13	$O_2NHCH_2CH_2CH_2NHNO_2$	″	120–160	27.8	11.18	140	3.0×10^{-4}	[9]
14	$CH_3CH_2CH_2CH_2NHNO_2$	″	120–170	26.6	10.15	140	1.5×10^{-4}	[10]
15	$NCCH_2CH_2NHNO_2$	″	140–180	28.6	11.13	140	1.0×10^{-4}	″
16	Nitrobenzene	Gas	410–480	69.7	17.3	400	4.7×10^{-7}	[11]
17	*para*-Dinitrobenzene	″	420–480	68.6	17.1	400	6.8×10^{-6}	″
18	*meta*-Dinitrobenzene	″	420–480	68.0	16.9	400	6.6×10^{-6}	″
19	*sym*-Trinitrobenzene	″	380–470	67.3	17.2	400	2.2×10^{-5}	″
20	$(O_2N)_3CCH_2N(NO_2)CH_3$	Solution	130–180	40.3	16.7	150	7.6×10^{-5}	[1]
21	$[(O_2N)_3CCH_2N(NO_2)CH_2]_2$	″	130–180	40.7	16.8	150	5.9×10^{-5}	″
22	$O_2NOCH_2CH_2ONO_2$ (nitroglycol)	Liquid				140	4.7×10^{-6}	[12]
23	$O_2NOCH_2CH_2CH_2ONO_2$	″	72–140	39.1	14.9	140	1.7×10^{-6}	[13]
24	$O_2NOCH_2CH(ONO_2)(CH_3)$	″	72–140	40.3	15.8	140	3.0×10^{-6}	″
25	$O_2NOCH_2CH(OH)(CH_2ONO_2)$	″	80–140	42.4	16.8	140	2.3×10^{-6}	″
26	$O_2NOCH_2CH_2CH_2CH_2ONO_2$	″	100–140	39.0	14.7	140	1.1×10^{-6}	″
27	$O_2NOCH(CH_3)CH(CH_3)ONO_2$	″	72–140	40.3	14.9	140	5.0×10^{-6}	″
28	$O_2NOCH_2CH_2OCH_2CH_2ONO_2$	″	80–140	42.0	16.5	140	1.9×10^{-6}	[14]
29	$O_2NOCH_2CH_2(NNO_2)CH_2CH_2ONO_2$	″	80–140	41.5	16.5	140	3.5×10^{-6}	″
30	$[(O_2NOCH_2)CH(ONO_2)CH(ONO_2)]_2$ (hexanitromannite)	″	80–140	38.0	15.9	140	6.3×10^{-5}	″
31	$(O_2NOCH_2)_4C$ (TEN)	″	145–171	39.0	15.6	140	9.3×10^{-6}	[15]
32	$(O_2NOCH_2)_2CHONO_2$	″	–	–	–	140	1.3×10^{-5}	[12]

tion centers, we consider the applicability of the above scheme and the character of secondary processes in the decomposition reactions of compounds from different classes.

RESULTS AND DISCUSSION

The table summarizes the kinetic characteristics of degradation for mono- and polyfunctional compounds, which provide an opportunity to compare k_n and k_0. These data were obtained for seven different classes of substances, which are considered below.

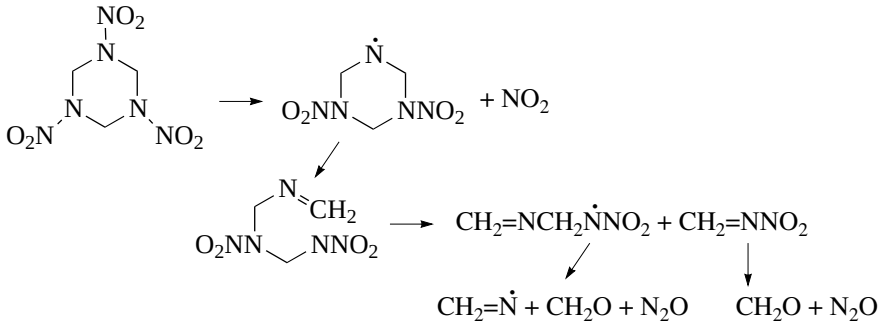
Difluoramino compounds. Previously [2], it was found that, for a great group of difluoramines (a portion of which is presented in the table), the rate constants and activation energies of the initial steps of degradation in a liquid state are independent of the number and arrangement of NF_2 groups in the molecules to within the experimental error. Thus, stepwise degradation in the series of polyfunctional difluoramines is evident and widespread. This conclusion is consistent with the reaction mechanism proposed previously [2] based on the studies of degradation in polar solvents. The reaction is the elimination of HF via the E_1 mechanism through the step of ion pair formation

$$RCH_2NF_2 \longrightarrow RCH_2N^+F|F^- \longrightarrow RCH = NF + HF.$$

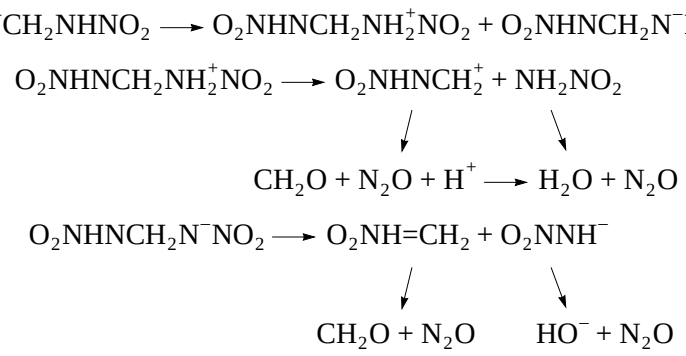
The N–F bond away from substituents is the reaction center; therefore, the substituents have almost no inductive effect. The elimination of HF leaves inert –C≡N or >C=NF groups, which have no effect on the reactivity of the remaining groups. Thus, difluoramino compounds meet the requirements of the scheme and provide support to conclusions drawn from it.

An analogous situation is observed in the *azide* series (nos. 8, 9). Similarly to difluoramines, there is no interaction of azide groups with each other because the substituents are spaced and, consequently, the induction effect through the C–N bond is weak. The activation parameters of GAP decomposition are independent of the number of units in GAP and coincide with the decomposition parameters of a monofunctional analog, propyl azide, which was studied in a gas phase. Other monoalkyl azides, in particular, ethyl azide and isopropyl azide [4], also exhibited rate constants of decomposition practically equal to that of GAP. It was found [16, 17] that the elimination of N_2 from azides was accompanied by the formation of imines, the subsequent conversion of which did not affect the remaining azide groups. Thus, unimolecular degradation was retained in the course of the overall reaction.

Secondary nitramines (Nos. 10, 11). Shaw and Walker [18] were the first to conclude, based on an analysis of published data, that the degradation of HMX in a gas phase was more rapid than that of dimethylnitramine (DMNA) by a factor of 4. This conclusion was also supported more recently [6]. Both of the compounds bear planar nitramine groups having the same reactivity. The degradation of HMX occurs in a single step. It is likely that a structural analog of HMX, RDX, for which the mechanism of secondary reactions was reliably established [19], undergoes degradation in the same manner. The rapid isomerization and degradation of a primary aminyl radical prevent the formation of stable intermediates in the decomposition of RDX and HMX.



Primary nitramines (nos. 12–15). Methylenedinitramine (MDNA) decomposes more rapidly than any monofunctional alkylnitramine by a factor of 2.5–3. It is likely that, in this case, there is no induction interaction between nitramine groups because propylenedinitramine exhibits the same rate of degradation as MDNA. At the same time, a small induction effect of substituents, which results in a change in the activation energy, in the series of monofunctional alkylnitramines was noted [10]. In this case, a compensation effect was observed, which suggests that the activation energy was determined inaccurately or the reaction occurred by a complex mechanism. If we take alkylnitramines as monofunctional analogs of dinitramines, we can formally conclude unambiguously that the latter undergo single-step degradation. The hypothetical mechanism of MDNA degradation [9] implies that the reaction proceeds through an equilibrium step of autoprotolysis and rapid degradation of ionic species.



In addition to this main path, a side alkylation reaction between ionic species occurs, and polymeric products are formed, which contain primary nitramine groups.

Aromatic nitro compounds (nos. 16–19). Nitrobenzene cannot serve as a monofunctional analog for polynitro benzene derivatives because of the intramolecular interaction of nitro groups. A change in the rate constant of gas evolution on going from nitrobenzene to TNB is due to a decrease in the activation energy; it is likely that this change can be explained by the resonance interaction of nitro groups [11] rather than by an increase in the number of these groups. Based on these limited data, we can draw only a preliminary conclusion that polynitrobenzenes undergo stepwise degradation.

Aliphatic nitro compounds (nos. 20, 21). A bifunctional nitronitramine (no. 21), although its molecule is saturated with active reaction groups, undergoes stepwise degradation: it is no different from its monofunctional analog (no. 20) in the reaction rate constant.

Nitro esters. Data for nos. 22–32 in the table suggest that the rate constants of the initial steps of liquid-phase decomposition of polynitro esters essentially depend on their structures. However, it was found [20–22] that the rate change in the polyester series could be completely explained by the induction effect of nitrate groups. This means that polynitro esters do not exhibit simple dependence of the rate constant on an increase in the number of reaction centers. Consequently, the degradation of all nitro esters, including nitroglycol and TEN, occurs via a stepwise mechanism.

The analysis performed demonstrates that stepwise degradation is typical of polyfunctional compounds from different classes. This degradation is adequately described by the proposed scheme. The reason for the appearance of stepwise processes even in the degradation reactions of molecules to form radicals is that C- and O-centered radicals rapidly decay in reactions with environmental molecules, and these bimolecular reactions (for example, hydrogen atom abstraction or disproportionation with NO_2) predominate over the unimolecular reactions of radicals under ordinary conditions [23]. These unimolecular reactions can result in the deep degradation of the entire molecule. The stepwise degradation of many polyfunctional compounds would be expected to be the predominant type of decomposition, especially, at high pressures or in a liquid phase.

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