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THERMAL STABILITY AND THERMAL DECOMPOSITION OF N-OXIDES

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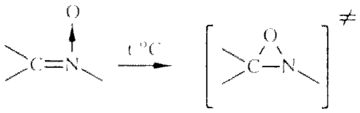
Kinetic manometric studies indicate that the first step in the thermal decomposition of a number of N-oxides is the formation of a cyclic activated complex. There is a correlation between the thermal stability of the compounds studied in the liquid phase and the charge on the oxygen atom of the N-oxide group calculated by the MPDP method. Autocatalysis of gas evolution from halogenopyridine N-oxides is explained by hydrogen halide autocatalysis. The limit of thermal stability for N-oxides is likely to be no greater than 270°C.

Heterocyclic compounds containing the N-oxide group as a plosive unit (i.e., a group providing explosive properties) are of interest as possible high energy substances. In this connection studies of the thermochemistry and the prediction of the thermal stability of N-oxides are of theoretical and practical interest.

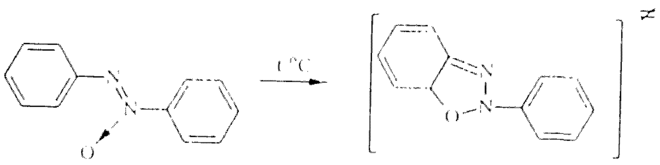
In this work we have attempted to discover the general characteristics of the initial step in the thermolysis and to predict the thermal stability limit for N-oxides on the basis of manometric studies. Table 1 contains Arrhenius parameters for thermal decomposition (E, lg A), the thermal stability limit (T_{st} °C at which the rate constant for decomposition $k = 1 \cdot 10^{-6}$ sec^{-1}), T the experimental temperature range and qO, the electronic charge on the oxygen atom of the N-oxide group calculated by the MPDP method with optimization of the molecular geometry. The data are from the present and previous studies [1-3].

The similarity of the kinetic parameters for gas phase and liquid phase thermolysis of the N-oxides studied and the negative entropies of activation for benzofuroxanes [1], pyridine N-oxides [2] and azoxybenzene [3] suggest that the first step in the thermolysis of these compounds is the formation of more ordered cyclic active intermediates:

for the heterocycles



and for azoxybenzene



The formation of similar intermediates suggests that the N – O bond is the reactive center for the initial steps of the thermolyses of the N-oxides studied. In fact the correlation of the rate constants for the liquid phase thermolysis of a series of pyridine-N-oxides with the calculated parameters of the N – O bond found previously [2] applies to a wider range of N-oxides. For example, the correlation of the thermal stability for the heterocycles I, II, IV, V, VII-XIV, XVIII and azoxybenzene in the liquid state (molten) with the calculated value of qO is well expressed by the equation:

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TABLE 1. Parameters for the N-Oxides Studied

№	Compound	mp, °C	Phase	T, °C	E, kJ mole^{-1}	lg$A$	T$_{st}$, °C	$-qO$	References
I	Benzofuroxane	72	g	260...290	165	12,5	193	0,2921	[1]
			l	110...150	152	12,9	147		[3]
II	4-Nitrobenzofuroxane	142	g	230...280	158	11,8	189	0,2611	[1]
			l	180...200	151	12,6	151		
III	5-Nitrobenzofuroxane	71	g	240...280	157	11,8	189	0,2657	[1]
IV	4,6-Dinitrobenzofuroxane	174	g	250...280	159	12,1	186	0,2149	[1]
			l	180...200	146	12,3	144		
V	5-Pyrido-[2,3-*c*]-furoxane	96	g	220...260	151	11,3	170	0,2301	[1]
			l	115...140	112	8,4	135		
VI	4-Amino-5-nitropyrido-[2,3-*c*]-furoxane	141	g	230...260	152	12,1	166	0,2643	[1]
VII	Pyridine-1-oxide	68	l	210...260	164	11,5	218	0,4223	[2, 3]
VIII	3-Methylpyridine-1-oxide	37	l	220...260	156	10,5	220	0,4278	[2, 3]
IX	4-Methylpyridine-1-oxide	187	l	190...230	172	12,9	205	0,4214	[2, 3]
X	2,6-Dimethylpyridine-1-oxide	–	l	200...235	156	11,1	202	0,4204	[2, 3]
XI	2,4,6-Trimethylyridine-1-oxide	31	l	210...250	161	11,4	211	0,4186	[2, 3]
XII	2,4,6-Trimethoxypyridine-1-oxide	109	l	210...230	152	11,1	192	0,4108	[2, 3]
XIII	3-Hydroxypyridine-1-oxide	190	l	195...220	151	11,3	182	0,4125	[2, 3]
XIV	4-Nitropyridine-1-oxide	164	l	165...200	131	10,1	151	0,3541	[2, 3]
XV	2,6-Dichloro-4-nitropyridine-1-oxide	168	s	120...150	144	13,6	112	0,2891	[2]
XVI	Azoxybenzene	36	l	200...230	151	10,1	218	0,4090	[3]
XVII	3-Bromo-4-nitropyridine-1-oxide	155	s	100...135	119	12,0	72	0,3624	
XVIII	1,2,2,5,5-Pentamethyl-4-phenyl-3-imidazoline-1-oxide	92	l	140...175	102	7,2	131	0,4053	
XIX	2,2,5,5-Tetramethyl-4-phenyl-3-imidazoline-1-oxide	82	l	130...200	169	15,1	148	–	
XX	2,2,5,5-Tetramethyldihydropyrazine-1,4-dioxide	305	s	200...235	165	10,1	216	0,4053	

$$T_{st} = -324.45\,qO + 60.76, \quad r = 0.76, \; s = 21.5$$

where r is the correlation coefficient and s is the mean squared deviation.

The largest difference between T_{st} calculated from this equation and the experimental value (61°C) apparently arises from steric factors which were not taken into account for the sterically hindered imidazoline XVIII.

Despite the complexity and the ambiguous nature of the effect of the phase on the kinetics and mechanism of the thermolysis of high energy substances containing nitrogen, a general tendency to increasing thermal stability with increasing charge on the N-oxide oxygen can be discerned in the series of compounds studied.

Consequently it is possible to predict the thermal stability of N-oxides from the calculated characteristics of the N–O bond.

The halogenopyridine-N-oxides XV and XVII have comparatively low thermal stabilities. The high initial rate of thermolysis, characteristic of autocatalysis, did not permit the determination of the Arrhenius parameters 4-chloropyridine-N-oxide [2]. These observations suggest halogen containing decomposition products are responsible for the autocatalysis. Model experiments on the thermolysis of pyridine-N-oxide at 270°C in the presence of equimolar amounts of various chlorides gave the following rate constants for the initial stage of thermolysis:

$$k\,(\mathrm{PyO}) = 2{,}8 \cdot 10^{-6}\ \mathrm{sec}^{-1};$$

$$k\,(\mathrm{PyO + NaCl}) = 2{,}0 \cdot 10^{-6}\ \mathrm{sec}^{-1};$$

$$k\,(\mathrm{PyO + NH_4Cl}) = 1{,}8 \cdot 10^{-5}\ \mathrm{sec}^{-1}.$$

In the presence of ammonium chloride, a source of hydrogen chloride, the rate of thermolysis of pyridine-N-oxide increased by an order of magnitude over the rate in the presence of sodium chloride (which does not give hydrogen chloride) which indicates that hydrogen halide is the source of the autocatalysis.

Comparison of the kinetic parameters for imidazolines XVIII and XIX indicates different mechanisms for the initial steps of thermolysis for N-oxides and nitroxyl radicals which will require further study.

These investigations show the simplest high energy model compounds have the greatest thermal stability. Introduction of the electron withdrawing nitro group decreases the charge on the N-oxide oxygen atom and the thermal stability. The upper limit for T_{st} is limited by the thermal stability of the simplest compounds and will evidently not exceed 270°C.

EXPERIMENTAL

The compounds studied were carefully purified by vacuum sublimation or recrystallization. Kinetics of thermolysis of the heterocycles II, IV, V, and XVII-XX were studies by a manometric method under isothermal conditions (± 0.2°C) in Pyrex Bourdon manometer reactors with volumes of 8-10 cm^3 using 0.2-0.5 g samples. Kinetic curves for the thermolysis of compounds II, IV, V, XVII, and XX are S-shaped. The thermal decomposition of compound XVIII follows first order kinetics to a large degree of conversion of the starting material. Rate constants for gas evolution were determined for the initial part of the decomposition curves to 1-2% conversion of the starting material. The Arrhenius parameters were calculated from 4-5 rate constants measured over the temperature limits given in Table 1.

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