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Kinetics of the Gas Phase Pyrolysis of Tetranitromethane[1]

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Reported herein are the results of our study of the pyrolysis of tetranitromethane (TNM).

Experimental Section

The 90.6-ml monel electrically heated, stirred flow reactor was identical with that described by Sullivan and Houser.[2] TNM vapor of 99% purity was mixed with helium and passed through the reactor at 1 atm total pressure and a TNM initial partial pressure of 1.09 mm (runs 1–23). The storage tank was repressurized with helium prior to run 24 giving an initial TNM partial pressure of 0.48 mm in the final eight experiments. The reactor was by-passed to permit analysis of the unreacted TNM. A sample of the gas stream from the reactor (or the by-pass) was periodically analyzed for TNM by introducing it into the helium carrier gas stream of a gas chromatograph by means of an unlubricated Beckman gas sampling valve. The reduction in TNM concentration with residence time in the reactor was followed chromatographically using a 3-ft column of 5% S.E.-30 silicone oil on Celite, 60–100 mesh, at room temperature and a thermal conductivity detector. The flow rates through the reactor were measured with a soap bubble flow meter connected to the exit stream. The measured flow rates and reactor volume were corrected to reactor temperature.

Mass spectrometric analysis of the decomposition products showed the presence of the species NO_2, NO, N_2O, and CO_2. The presence of NO_2 and CO_2

(1) This work was supported by the U. S. Air Force and the Advanced Research Projects Agency under Contract No. AF04(611)-9380 and ARPA Order No. 24.

(2) J. M. Sullivan and T. J. Houser, *Chem. Ind.* (London), 1057 (1965).

was further substantiated by infrared spectrometry. However, attempts to establish a mass balance for these species proved unsuccessful.

Results

The results obtained for the thermal decomposition of TNM over the temperature range 170–223° are presented in Table I. The rate equation for a simple order, single-reactant reaction in a stirred flow reactor is

$$k_n = (P^0 - P)/(P^n\tau) \quad (1)$$

where P^0 and P are the partial pressures, respectively, of the reactant in the gas streams entering and leaving the reactor, τ is the *average* residence time in the reactor, and n is the order of the reaction.[3,4] It is of interest to note that for a first-order reaction in a stirred flow reactor a plot of $1/P$ *vs.* τ will yield a straight line, whereas such a plot will be linear only for a second-order reaction in a plug flow or static reactor.

Table I: Experimental Kinetic Data for the Pyrolysis of Gaseous Tetranitromethane

Run no.	Temp, °C	τ, sec	Fraction reacted, α	k_1, sec^{-1}	k_1^A, sec^{-1}
17	170.0	99.2	0.171	0.00208	0.00222
18		169.5	0.249	0.00196	
19		172.9	0.307	0.00256	
20		174.0	0.283	0.00227	
21	181.2	123.5	0.452	0.00668	0.00680
22		126.1	0.455	0.00662	
23		128.0	0.479	0.00719	
1	186.9	14.3	0.154	0.0127	0.0130
2		27.0	0.265	0.0134	
3		41.5	0.355	0.0133	
4		43.7	0.340	0.0118	
5		54.7	0.416	0.0130	
6		63.0	0.468	0.0140	
10	192.2	13.4	0.229	0.0221	0.0232
11		16.9	0.274	0.0224	
12		23.4	0.310	0.0192	
13		24.3	0.376	0.0248	
14		36.8	0.477	0.0248	
27	198.0	9.69	0.266	0.0375	0.0382
28		9.78	0.276	0.0390	
15	206.7	13.7	0.541	0.0856	0.0856
16		14.1	0.546	0.0855	
7	213.0	5.98	0.474	0.151	0.144
8		6.70	0.475	0.135	
9		7.07	0.510	0.147	
24	215.0	4.74	0.414	0.149	0.150
25		4.89	0.442	0.162	
26		5.02	0.410	0.144	
29	223.2	2.43	0.438	0.320	0.328
30		2.50	0.455	0.334	
31		2.71	0.417	0.264	

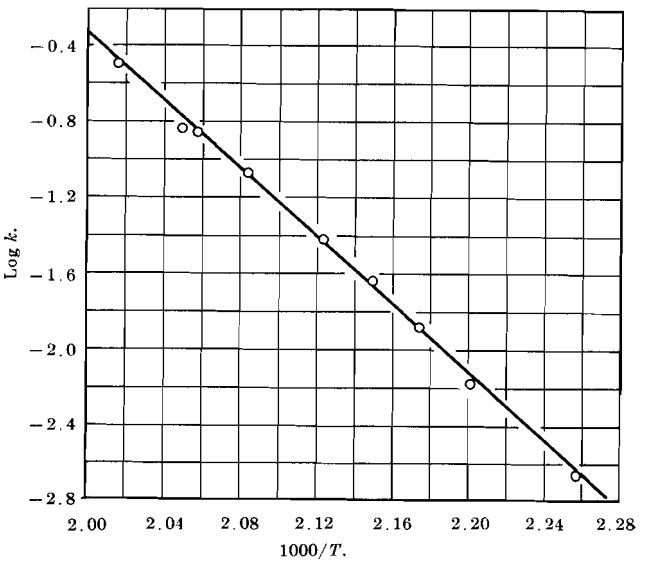


Figure 1. Arrhenius plot for the gas phase pyrolysis of tetranitromethane.

The first-order nature of the decomposition of TNM is illustrated in Table I, particularly with the data obtained at 186.9°. It can be shown from eq 1 that a plot of $\alpha/(1 - \alpha)$ *vs.* τ, where α is the fraction reacted, should be linear for a first-order reaction. The rate constant, k_1, from each experiment is listed in Table I. The best first-order rate constant, k_1^A, at each temperature, obtained from the slope of the best line from an $\alpha/(1 - \alpha)$ *vs.* τ plot, is given in the last column of Table I. The Arrhenius plot (Figure 1) of these rate constants yields the rate expression

$$k_1 = 10^{17.53} \exp(-40{,}875/RT)\ sec^{-1} \quad (2)$$

The uncertainty in activation energy is about 1.2 kcal/mole.

The possibility of a heterogeneous contribution to the rates obtained in this study has not been completely eliminated. It appears, however, from the high preexponential factor and the magnitude of the activation energy, that the reaction is homogeneous.

Discussion

We believe that the kinetic parameters obtained indicate that the rate-determining step is the rupture of a single C–N bond

$$(NO_2)_3C\text{–}NO_2 \longrightarrow (NO_2)_3C\cdot + NO_2 \quad (3)$$

(3) W. C. Herndon, *J. Chem. Educ.*, **41**, 425 (1964).

(4) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1956, p 185.

This is in agreement with Benson[5,6] who has suggested that for bond rupture within a molecule a "high" preexponential factor of 10^{15} to 10^{18} sec^{-1} is to be expected. Reaction 3 is then followed by further bond rupture or, more likely, by an isomerization process in which an oxygen atom is transferred to the unsaturated carbon atom.

Since the reverse of reaction 3 should have nearly a zero activation energy, the measured activation energy for the pyrolysis of TNM is approximately equal to the dissociation energy of the first C–N bond in TNM if reaction 3 is rate determining. Reaction 3 will be rate determining if the radical formed reacts much more rapidly by another path than by recombination with NO_2. The only other apparent mechanism which could give first-order kinetics independent of the buildup of product NO_2 would be one in which reaction 3 was rapidly reversible and the rate-determining step involved the reaction

$$NO_2 + (NO_2)_3C\cdot \longrightarrow \text{products} \qquad (4)$$

In this case, the measured activation energy would be equal to the dissociation energy of the C–N bond plus the activation energy of reaction 4.

Marshall, Borgardt, and Noble[7] have reported kinetic parameters for the condensed-phase pyrolysis of hexanitroethane (HNE). In the case of solid HNE, the preexponential factor was $10^{18.6}$ and the activation energy 38.9 kcal/mole. Within experimental error, this activation energy is the same as that for gaseous TNM.

It was postulated for solid HNE that the rate-determining step is the simultaneous cleavage of two C–N bonds to give a diradical intermediate.[7] This was based partly on the high preexponential factor of $10^{18.6}$ which was attributed to the unfreezing in the activated complex of the carbon–nitro system (however, the uncertainty in this preexponential factor is a factor of 10^3 to 10^4 since the stated average deviation in the activation energy is 10%). Our results with TNM (one carbon atom) indicate that unfreezing of the carbon–nitro system is not required to obtain a high preexponential factor. The mounting evidence that bond rupture yielding two polyatomic radicals is associated with a "high" Arrhenius factor,[5,6] supported by unpublished work from this laboratory, makes it apparent that the kinetic results reported for solid HNE[7] fit equally well a simpler mechanism in which the rate-determining step is the rupture of the initial C–N bond.

(5) S. W. Benson, *Ind. Eng. Chem.*, **56**, 18 (1964).

(6) S. W. Benson and W. B. DeMore, *Ann. Rev. Phys. Chem.*, **16**, 426 (1965).

(7) H. P. Marshall, F. G. Borgardt, and P. Noble, Jr., *J. Phys. Chem.*, **69**, 25 (1965).