it is evident that this group is exposed to solvent. Hence the apolar substituents attached to the amide must also be in contact with solvent. In aqueous solution, in the local environment of the macromolecule with its many apolar groups, K_w should be significantly affected. If K_w is reduced in the neighborhood of the polymer, then $k_{\min}$ would be definitely decreased, as is indicated by eq 6 as well as by experiments in simpler systems.[4] In addition if the solvent character is changed at the polymer surface, the concentrations of the charged intermediates II and III would be reduced, and hence k_D and k_{OD} would also be lowered. In consequence the net, observed rate would be decreased even further.

Thus from these experiments with a synthetic polymer it seems apparent that the nature of the solvent in the neighborhood of a residue of a macromolecule is different from bulk solvent and that this difference may have a profound effect on the reactivity of constituent residues. It seems likely, therefore, that similar phenomena would be encountered in protein solutions and hence that hydrogen–deuterium exchange in these biopolymers would also be affected by the state of the solvent in the local environment.

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Very Low Pressure Pyrolysis. II. Decomposition of Nitropropanes[1]

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Contribution from the Department of Thermochemistry and Chemical Kinetics, Stanford Research Institute, Menlo Park, California. *Received May 31, 1967*

Abstract: The technique of very low pressure pyrolysis (vlpp) has been applied to 1- and 2-nitropropane. Pyrolysis was carried out at pressures from about 2 to 10 μ and at temperatures ranging from 650 to 1100°K, in a quartz vessel with residence time of about 0.4 sec. Both isomers gave the same primary reaction products, HNO_2 + C_3H_6, with HNO_2 decomposing further at the reaction conditions. The first-order rate parameters agreed well with those estimated from low-temperature studies. The activation energies and thermochemistry show that the reverse reaction, the exothermic addition of HNO_2 to an olefin, follows the Markovnikov rule. Addition of the NO_2 group to the CH_3-bearing C atom is favored by 7.2 kcal/mole of activation energy.

Several studies of pyrolysis of nitropropanes were made during the period 1950–1960.[2–6] The most recent of these was made by Smith and Calvert[6] (SC) whose product analyses showed that propylene production from the pyrolysis of 2-nitropropane (2-NP) followed a first-order rate law with $k = 1.11 \times 10^{11-39.3/\theta}$ sec^{-1} ($\theta = 2.303RT$ in kcal/mole). They proposed that HNO_2 was split off from the parent compound with the H coming from the vicinal carbons. Previous workers had proposed, in addition, either C–NO_2 bond breaking, followed by a chain reaction,[2,4] or HNO elimination with the H coming from the geminal position.[5] In all cases, there was secondary oxidation by HNO_2 and its decomposition products ($H_2O + NO + NO_2$).

Some doubt has remained about the nature of the primary process since many of the products of reaction can only be accounted for under the assumption of secondary reaction.[7] The five-center split-out of HNO_2 has not appeared to be a very attractive mechanism in comparison with the simpler C–NO_2 bond break. The HNO elimination appears unlikely on energetic grounds.

Cottrell, Graham, and Reid[3] (CGR) briefly reported the results of some 1-nitropropane pyrolyses. They found that the mechanism probably proceeded with production of propylene and HNO_2, but with an activation energy of about 50 kcal/mole. Their quoted rate constant at 388° was close to 4×10^{-3} sec^{-1}. No correction was made for the appreciable surface reaction observed in the system, and their reported A factor of 10^{13} sec^{-1} should have been a factor of 10 higher to agree with their reported data and activation energy. Gray, Yoffe, and Roselaar[4] (GYR) have also reported on 1-nitropropane pyrolysis, but the results of their experiments were inconclusive. Fréjacques[2] also pyrolyzed the nitropropanes, but his data are probably affected by chain-reaction effects.

The technique of very low pressure pyrolysis[8] (vlpp) is appropriate for determining the primary process in a pyrolytic system, since pyrolyses are carried out at pressures so low that secondary reactions can be either

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[1] This work was supported in part by the National Aeronautics and Space Administration, under Contract NAS7-472.

[2] C. Fréjacques, *Compt. Rend.*, **231**, 1061 (1950).

[3] T. L. Cottrell, T. E. Graham, and T. J. Reid, *Trans. Faraday Soc.*, **47**, 1089 (1951).

[4] P. Gray, A. D. Yoffe, and L. Roselaar, *ibid.*, **51**, 1489 (1955).

[5] K. A. Wilde, *Ind. Eng. Chem.*, **48**, 769 (1956).

[6] T. E. Smith and J. G. Calvert, *J. Phys. Chem.*, **63**, 1305 (1959).

[7] SC found that the ratio of rates of decomposition of 2-NP to the rate of C_3H_6 formation varied from about 9 (250°) to 1.6 (337°). Minor products included acetone (~6%), acetonitrile (~7%), and CO + CO_2 (4%).

[8] S. W. Benson and G. N. Spokes, *J. Am. Chem. Soc.*, **89**, 2525 (1967).

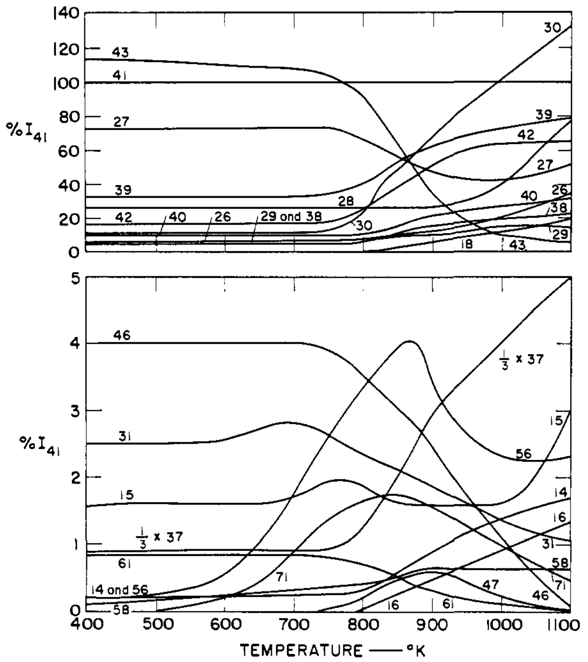

Figure 1. Mass spectra of the products of pyrolysis of 1-nitropropane in a 9000-collision reaction vessel. Ion intensities are referred to mass 41 amu. Curves are constructed by drawing lines through points obtained at the following temperatures: 473, 523, 573, 580, 615, 690, 773, 793, 823, 873, 893, 896, 900, 908, 1010, and 1100°K. The upper part of this figure (and Figure 2) portrays variation of the more intense peaks; the less intense ones are given in the lower part of the figures. Scatter of experimental points is about 5% for the more intense peaks and up to 20% for the weaker ones.

eliminated or minimized. The present work was undertaken in order to clarify the primary process in the pyrolysis of nitroalkanes and to establish the appropriate Arrhenius parameters.

Experimental Section

Experimental procedure followed that outlined elsewhere.[8] Nitropropanes were distilled from practical grade material, using only the central fractions. The resultant material was close to 96% pure; the remaining 4% was due to the isomeric material as judged by vpc (6-ft column of 15% Carbowax 20M + 2% KOH on Chromosorb W, 30–60 mesh at 160°). Gases were stored in separate 5-l. bulbs at a pressure of about 2 torr. A variable leak controlled the flow rate into the cylindrical fused silica vessel. Typical gas flows were 5×10^{15} to 10^{16} molecules/sec. The reaction temperature was controlled to about ±5°. The internal diameter of the reactor was 2.2 cm and its length about 10 cm; the exit aperture, through which gases escaped into the mass spectrometer, was 1 mm in diameter. On the average, molecules make about 9000 collisions with the reactor walls before escaping into the mass spectrometer. The mean free path for gas–gas and gas–wall collisions is about 1 cm with a gas flow of 10^{16} molecules/sec. At a flow rate of 5×10^{15} sec^{-1} there are approximately equal numbers of gas–gas and gas–wall collisions during the residence time of an average molecule.

Mass spectra of the product gases were obtained using a quadrupole mass spectrometer equipped with a particle multiplier tube. Output current was recorded with an oscilloscope–Polaroid camera combination.

Calibration runs were made by taking mass spectra of mixtures of C_3H_6 with 1-NP, C_3H_6 with 2-NP, and C_3H_6 by itself.[9]

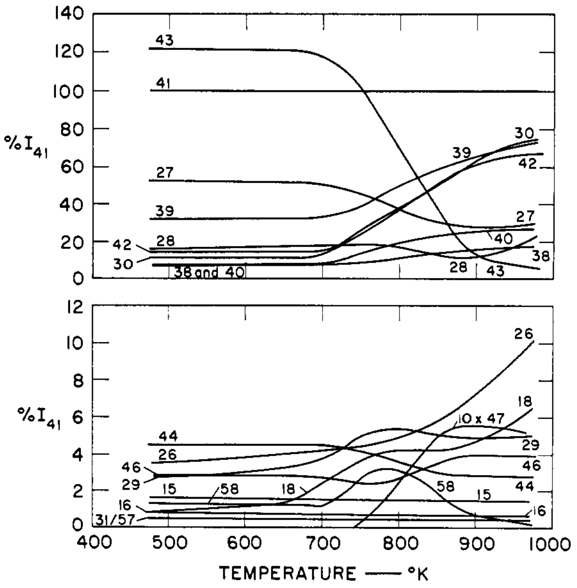

Figure 2. Mass spectra of the products of pyrolysis of 2-nitropropane. Temperatures at which experimental points were obtained were 470, 520, 653, 773, 878, 973, and 978°K.

Results

The mass spectra are presented in Figures 1 and 2. In each case, the intensity of the ion peaks is quoted relative to mass 41 (which is prominent in both parent and product compounds); the mass peak at 41 amu is given the arbitrary value 100. Background mass spectra were subtracted out, using 32- and 45-amu peaks as reference for air and hydrocarbons, respectively.

All of the major peaks are included in the upper parts of Figures 1 and 2 and most of the minor peaks in the lower parts of those figures. The parent peak at 89 amu is less than 2×10^{-3} of mass peak 41. The absence of background interference at 47 amu permits us to say with some confidence that HNO_2 is a significant, although small, product peak. NO_2 produced does not exceed 20% of the C_3H_6, and acetone (as judged by the 58-amu peak) is always $\leq 4\%$ of C_3H_6.

Variation of gas flow has little effect on the mass spectra. A twofold increase of gas flow at 500° led to a change of less than 10% in rate constant for 2-nitropropane, and a fivefold increase at 620° led to approximately 30% increase of rate constant for 1-nitropropane. This indicates that we are looking at primary reactions and that chain reactions are unimportant.

Experiments on 1-NP were done at a high temperature of 1100°K as compared with a maximum of 970°K for 2-NP. Differences in the mass spectra of the highest temperature runs are attributed to further decomposition in the case of 1-NP. However, the mass spectra at 970°K for the two nitropropanes resemble one another closely.

Run reproducibility was satisfactory on a day-to-day basis. Rate constants were within the scatter of those obtained previously.

Interpretation of the Data

The first point of interest is that both compounds appear to form similar product spectra and that the

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[9] Important peaks in the C_3H_6 spectrum are

amu	43	42	41	40	39	38	37	27	26
$\%I_{41}$	2	66	100	28	80	20	18	41	16

Relative sensitivities at 41 amu for equal molecular flows of propylene and 1-NP are found to be $S^{41}_{\text{prop}}/S^{41}_{1\text{-NP}} = 0.61$ and for 2-NP, $S^{41}_{\text{prop}}/S^{41}_{2\text{-NP}} = 0.98$.

Table I. Decomposition of 1-Nitropropane[a]

	Temperature, °K									
	690	773	773	793	823	873	893	893	896	900
I_{43}/I_{41}	1.07	1.00	0.983	0.944	0.739	0.449	0.414	0.394	0.369	0.545
I_{42}/I_{41}	0.175	0.20	0.21	0.24	0.32	0.47	0.50	0.48	0.51	0.52
k_{uni}, sec^{-1}	0.05	0.32	0.40	0.64	1.94	6.3	7.5	7.7	8.9	9.7

	Temperature, °K									
	902	902	902	902	907	908	1006	1013	1100	1100
I_{43}/I_{41}	0.358	0.328	0.336	0.366	0.322	0.318	0.100	0.094	0.058	0.059
I_{42}/I_{41}	0.51	0.52	0.54	0.52	0.51	0.51	0.64	0.64	0.64	0.65
k_{uni}, sec^{-1}	9.2	10.4	10.5	9.2	10.4	10.5	56	60	117	106

[a] The terms I_{41}, I_{42}, and I_{43} refer to the mass spectrometer signals at 41, 42, and 43 amu, respectively; k_{uni} is the first-order unimolecular rate constant calculated from the product of the ratio of propylene to parent compound and the calculated escape rate constant for the parent compound.

Table II. Decomposition of 2-Nitropropane[a]

	Temperature, °K														
	773	773	773	773	773	773	878	878	878	973	973	978	978	978	978
I_{43}/I_{41}	0.875	0.86	0.84	0.856	0.837	0.825	0.209	0.201	0.189	0.0709	0.087	0.068	0.056	0.074	0.061
k_{uni}, sec^{-1}	0.81	0.87	0.93	0.87	0.93	0.96	11	12	13	53	41	57	74	51	67
Gas flow (10^{15} molecules/sec)	4.5	4.5	8.0	8	10	10	10	10	10	10	10	10	10	10	10

[a] See corresponding footnote in Table I.

ratio of rates of decomposition of the 1-$C_3H_7NO_2$/2-$C_3H_7NO_2$ is about the same at temperatures differing by about 25°. The 1-$C_3H_7NO_2$ decomposes about one-third as fast as its isomer at any common temperature.

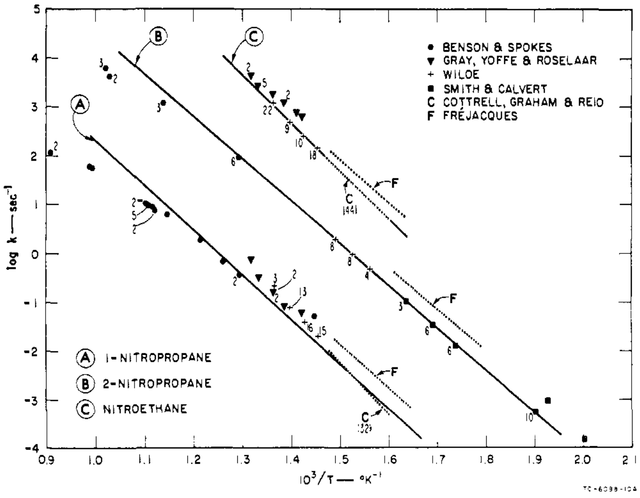

Figure 3. Arrhenius plots of available data on the pyrolysis of nitroethane and nitropropanes. Small numerals adjacent to data points or lines refer to experimental weight where this is different from unity. Important note: The rate constants for 2-nitropropane and nitroethane have been increased by 10^2 and 10^4, respectively, in order to present the data more clearly.

The mass spectra of the products can be accounted for by an initial reaction step, which yields C_3H_6 and HNO_2. The HNO_2 decomposes to give H_2O, NO, and NO_2.

$$C_3H_7NO_2 \longrightarrow C_3H_6 + HNO_2$$

$$2HNO_2 \longrightarrow H_2O + NO + NO_2$$

From the ratio of C_3H_6 to $C_3H_7NO_2$ in the gases emergent from the reactor, together with the reactor geometry, we immediately derive the unimolecular decomposition rate from the formula $k_{uni} = k_{ea}N(C_3H_6)/N(C_3H_7NO_2)$. The escape rate constant[10] is k_{ea} sec^{-1}, $N(X)$ is the number of molecules of X escaping from the reactor per unit of time, and the ratio $N(C_3H_6)/N(C_3H_7NO_2)$ is given by a simple formula involving the relative intensities of the 41, 42, and 43 mass peaks.[11] (It should be noted that free-radical processes which lead to propylene formation are unlikely to occur.)

The decomposition rate constant *vs.* temperature is given in Tables I and II. These data are obtained by comparing the relative peak heights at masses 41, 42, and 43 amu with the relative intensities of those peaks for standard mixtures of the appropriate nitropropane and propylene. Isotopic peaks are taken into account. Arrhenius plots of our rate constant data are included in Figure 3.

We thank a referee for calling our attention to the impurity problem. Limitations of time and cost prevent us from correcting all the rate constant data to take into account the fact that isomeric impurities amounted to 4%. The corrections are small, however, and amount to a maximum of about 10% in the case of the 1-NP decomposition rate constant at low temperatures, and to about 20% for the 2-NP at high temperatures (the error is only about 10% at lower temperatures for 2-NP). We may also note that systematic errors of this type could have played an interfering role in experiments of other workers.

It is possible that some error can arise if species other than $C_3H_7NO_2$ or C_3H_6 contribute to the mass spectrum at 41, 42, and 43 amu. Both nitropropanes give rise to decomposition products which have a small ($\sim 0.035 I_{41}$) 44-amu peak. If this peak derives from a

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(10) The rate of escape of nitropropane molecules from the reactor, k_{ea}, is given by $k_{ea} = 8.74 \times 10^{-2}\sqrt{T}$ sec^{-1}, so that the average residence time is, typically, 0.4 sec.

(11) Only peaks 41 and 43 were used in evaluating the decomposition rate constants of 2-nitropropane.

hydrocarbon (or an oxygenated hydrocarbon) containing several hydrogens, one may expect that a mass 43 peak of similar intensity (within a factor of 3) would be associated with it. No allowance can be made for such a contribution to the 43 peak in the absence of further information regarding product mass spectra, other than C_3H_6 and HNO_2. Neglect of such contributions leads to too big a 43/41 ratio, and the effect of this is that the apparent rate constant is lower than the real one. We estimate that only the data at 700° in the case of the 2-nitropropane and at 827° in the case of the 1-nitropropane can be noticeably affected in this way.

Experiments at various presssures at constant temperature show that free-radical reactions (*i.e.*, secondary reactions) interfere only slightly with our measurements.

We show later in a separate experiment on the HNO_2 mass spectrum that very little of the HNO_2 produced in these nitropropane decomposition reactions survives the high temperature of the reaction chamber. This is inferred from the small size of the mass 47 peak in the reaction product.

There are some interesting points of detail in the 1-nitropropane product mass spectra. First, as the temperature increases from 500 to 750°K, minor mass peaks at 71 and 56 amu rise from 0 and 0.25%, relative to I_{41}, to 2 and 3.5%, relative to I_{41}. The peaks reach a maximum between 770 and 950°K, but fall rapidly to 0.4 and 2.8% as the temperature rises to 1100°K. These changes in the heights of these peaks with temperature are different from those of the major product peaks, namely, 30, 39, 42 amu, and may be explained in one of two ways. One involves the assumption that the peaks are generated by the parent compound. The fragmentation pattern changes rapidly with amount of internal energy (some fraction of the molecules in the ionizer may not have cooled down vibrationally to the mass spectrometer temperature). The alternative view is that these peaks could be associated with nitropropylene and nitroethylene, produced perhaps by free-radical attack on the parent compound.

An Experiment on the Mass Spectrum of HNO_2

An attempt was made to detect a contribution of the mass spectrum of HNO_2 to the peak at 47 amu.

A mixture of H_2O, NO, and NO_2 was made and stored in a 5-l. storage vessel (3.8 torr of H_2O, 2.2 torr of NO, and 2.2 torr of NO_2). We estimate that this mixture should have contained about 1% HNO_2 in equilibrium at room temperature. The gas was passed through a variable leak consisting of a tungsten wire inserted into a slightly larger diameter capillary (wire diameter $\sim$0.115 cm, capillary diameter $\sim$0.127 cm, length of wire in capillary $\sim$5 cm). The pressure dropped on expansion into the glass inlet tubing to a pressure of about 0.1 torr and, after traveling through about 10 cc of this glass tubing and a 3 cm length of 0.5 mm i.d. capillary, the gases entered the reactor (estimated residence time at 0.1 torr in the inlet tubing $\sim$2 sec). In spite of these pressure reductions and a final reduction to mass spectrometer pressure ($\sim 8 \times 10^{-6}$ torr), a significant contribution (about 1% of the mass 30 peak) was noted at mass 47 amu. The mass 46 amu peak (NO_2^+) was typically ten times greater than the 47-amu peak, and the 30-amu peak ten times greater than the 46-amu peak (for NO_2 alone, $I_{46}/I_{30} = 0.19$).

On raising the (9000 collisions) reactor temperature to 600° and above, the 47-amu peak (presumably HNO_2^+) decreased to within 10% of the background value (that is, to the background value within the uncertainty of the measurement). This experiment shows that the HNO_2^+ peak is probably not formed by an ion–molecule reaction. It also indicates that the HNO_2 is unstable at high temperatures, although the reaction

$$2HNO_2 \longrightarrow H_2O + NO + NO_2$$

cannot proceed homogeneously in the above experiment since the HNO_2 partial pressure is too low.

The equilibrium amount of HNO_2 at 0.1 torr pressure of mixture (in the inlet tubes to the mass spectrometer) would be about 10% of its value at 8.2 torr pressure of mixture in the storage vessel. This fact and the fact that the 47-amu mass peak is, relatively speaking, so large indicate that the reaction which leads to the equilibrium

$$0.5(H_2O + NO_2 + NO) \rightleftarrows HNO_2$$

involves a step which is slow (compared with 2 sec) at the low pressures (0.1 torr) in the transfer system.

The small size of the 47-amu peak observed in the nitropropane decomposition product mass spectra therefore means that there is only a small concentration of HNO_2 in the effluent gases and suggests that HNO_2 is at too low a concentration to react with itself during the nitropropane pyrolysis experiments.

Discussion

The mass spectra obtained in our low-pressure reactor show that the primary decomposition mechanism for both nitropropanes involves propylene production, and we conclude that this comes about by a simple unimolecular split of HNO_2 from the parent molecule. Our estimates, using RRK (Rice, Ramsperger, Kassel) theory, show that at lower temperatures (around 500°) the decomposition will proceed at a rate approximately equal to the high-pressure rate, but that falloff will occur in our reactor at the higher temperatures. The increase of rate constant at the higher gas flows may be explained by the increased rate of gas–gas collisions, and hence reduced amount of falloff. The observed behavior of the rate constants obtained in our vlpp experiments concurs with these predictions.

We find that at 500° our measured rate constant for 2-nitropropane decomposition is exactly equal to that calculated by extrapolation of the low-temperature (255–337°) Arrhenius plots of SC and the 380° results of Wilde.[5]

If we assumed that the elimination of HNO_2 from the normal nitropropane proceeded with the same activation energy as from the 2-nitropropane, then we would infer from our results that the Arrhenius *A* factors for the decomposition of the two isomers would differ by a factor of 2.6. This compares with the value of 3, which would be expected on statistical grounds since 2-NP had three times as many available hydrogen atoms as 1-NP. The Arrhenius form of the rate constant $10^{10.62-39.3/\theta}$ sec^{-1} would fit the 1-nitropropane data quite satisfactorily. These rate parameters predict a rate constant of 4×10^{-3} sec^{-1} at 388°, precisely equal to that reported by CGR and only slightly less than the rate constants obtained by other workers.[2,4,5] It should be noted that our rate constants are specifically related to propylene production, whereas the rate constants of the other workers, with the exception of SC, refer to an over-all reaction rate, including chain and heterogeneous components. In spite of the superficial agreement between our rate constant data and those of others, we favor a slightly different set of Arrhenius parameters, as discussed below.

Presented in Figure 3 are Arrhenius plots of all the available data on the pyrolysis of three nitroalkanes.

Our higher temperature runs were in a regime closely approaching falloff. We do not yet have the theoretical capability of handling the rate constant data to extrapolate to the high-pressure limit in this regime. Our lower temperature rate constant data are, however, useful in giving a high-temperature anchor point for our Arrhenius plots of the available literature data on the 1-nitropropane and 2-nitropropane decompositions.

For 2-nitropropane, there is excellent agreement among SC, Wilde, and ourselves (our higher temperature points are increasingly subjected to falloff). The fact that this agreement exists gives us confidence in our method and in the correctness of the proposed mechanism. The Arrhenius form of the rate constant is $k(\text{2-NP}) = 10^{11.3-40/\theta}$ sec^{-1} ($\theta = 4.575T$).

We now turn to 1-nitropropane. Here, greater ambiguity exists in the correct location of the appropriate Arrhenius line. Certainly the preponderance of the low-temperature data favors a higher activation energy. In drawing the line, we have, however, used our own and the CGR rate constant data as anchor points. If heterogeneous, or chain, effects disturbed the work of CGR, then a line with greater negative slope would be applicable; however, an even greater slope than this has, as will be considered later, special implications regarding the relation between the Markovnikov and the anti-Markovnikov addition of HNO_2 to C_3H_6. The Arrhenius form of the rate constant data for 1-NP decomposition is $k(\text{1-NP}) = 10^{11.5-42/\theta}$ sec^{-1}.

The nitroethane rate constant parameters obtained from the graph are $k(\text{NE}) = 10^{12.4-45/\theta}$ sec^{-1}. Here again, however, systematic uncertainties in the rate constant data will lead to uncertainties in the Arrhenius parameters. We are thus hesitant to weight these results too heavily.

The data of Fréjacques and GYR provide, we think, upper limits to the rate constant data in each case. Fréjacques' work must have involved appreciable contribution by a chain reaction component. The work of GYR was done in a flow system; insufficient detail was given in their paper to ascertain whether the flow was plugged flow or stirred flow—a factor which may be important in evaluating their rate constant data at high per cent decomposition. We note that with 10- and 20-sec residence times and high percentage conversion, the decomposition rate constant is usually low (if plug flow is assumed). Chain reaction may lead to too high a rate at low conversion levels due to the fact that there is a higher nitro compound partial pressure at the lower conversions. The 40% ethylene in the products of nitroethane pyrolysis at 477.3° suggests the possibility that as much as 40% of the reaction was proceeding through HNO_2 elimination. Reliance on the corrected data point ($10^3/T = 1.333$, $\log k = -0.94$) would, together with CGR's data (uncorrected for chain), yield an activation energy of only 40 kcal/mole. A compromise value of 43 ± 2 kcal/mole for this parameter seems reasonable.

Our suggested values for the Arrhenius parameters of the three nitro compounds are given in Table III. It is understood that positive (negative) deviations of E are likely to be associated with negative (positive) deviations of $\log A$. Errors are difficult to estimate when using data obtained from several sources. The estimates were made using a transparent ruler and are half of the visually estimated 95% confidence limit values.

Table III. Experimental Arrhenius Parameters for Unimolecular Decomposition of Nitroethane and Nitropropanes to Olefins and Nitrous Acid

Compound	Log A, log sec^{-1}	E, kcal/mole
Nitroethane	11.75 ± 0.6	43 ± 2
1-Nitropropane	11.5 ± 0.6	42 ± 2
2-Nitropropane	11.3 ± 0.2	40 ± 0.5

From the ΔH_f values of 1-nitropropane and 2-nitropropane,[12] we may estimate the activation energy difference for addition reactions of HNO_2 to C_3H_6 to give either 1-nitropropane or 2-nitropropane. We have included the nitroethane data together with those for the nitropropanes in Table IV. We estimate that the average value of ΔC_p for products and reactants is close to zero over the temperature interval 298–800°K. We observe that Markovnikov addition is favored over anti-Markovnikov addition by 7 kcal/mole (HNO_2 is considered H^+X^-).

Table IV. Thermochemistry and Activation Energies for HNO_2 Addition to Olefins and the Reverse Reaction

Reaction	$\Delta H_{f,298}$[a]	ΔE_{800}[b]	E_{decomp}[c]	E_{add}[d]
$HNO_2 + C_3H_6 \rightarrow \text{1-}C_3H_7NO_2$	−15.7	14.7	42	27.3
$HNO_2 + C_3H_6 \rightarrow \text{2-}C_3H_7NO_2$	−20.8	19.8	40	20.2
$HNO_2 + C_2H_4 \rightarrow C_2H_5NO_2$	−18.4	17.4	43	27.6

[a] $\Delta H_{f,298}$ is calculated using JANAF and group values. [b] ΔE_{800} is the energy difference between products and reactants at 800°K ($\sim \Delta H_f - R\Delta T$). [c] E_{decomp} is the activation energy for unimolecular decomposition of the nitroalkane. These values are experimental ones derived from consideration of available rate constant data. [d] E_{add} is calculated from ΔE and E_{decomp}.

Benson and Haugen[13] have recently reviewed the analogous additions of HX to olefins (where X = F, Cl, Br, I) and have shown that, in general, there is in these cases a similar difference in the activation energies of the Markovnikov and anti-Markovnikov additions (about 5–8 kcal/mole), and that the activation energy for addition to ethylene is approximately the same as that for anti-Markovnikov addition to propylene. If then a similar model is appropriate for X =

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(12) R. C. Cass, S. E. Fletcher, C. T. Mortimer, P. G. Quincey, and H. D. Springall, *J. Chem. Soc.*, 958 (1958).

(13) S. W. Benson and G. R. Haugen, *J. Am. Chem. Soc.*, **87**, 4036 (1965).

NO_2, we would expect E_a for HNO_2 addition to C_2H_4 to be the same as that for anti-Markovnikov addition to C_3H_6. (ΔC_p for the nitroethane reaction is also close to zero.) Taking E (decomposition) for the nitroethane as 43 ± 2 kcal/mole, we see that addition of HNO_2 to C_2H_4 has an activation energy of 27.5 ± 2 kcal/mole and that this is indeed the same as for anti-Markovnikov addition of HNO_2 to C_3H_6.

There are a number of problems raised by the present work that we are unable to resolve at the moment. We note that HNO_2 in the products reaches a maximum at about 50% decomposition and that the amount of HNO_2 produced is too small. Under our reaction conditions there is no rapid, homogeneous path for HNO_2 decomposition. The implication is that HNO_2 is removed by a wall reaction or else by the bimolecular route

$$2HNO_2 \rightleftharpoons NO + NO_2 + H_2O$$

The small amounts of HNO_2 present in the products preclude establishment of this equilibrium by a bimolecular reaction having any activation energy. The equilibrium is known to be rapidly achieved at 298°K,[14] but all signs point to a surface-catalyzed reaction that should not be favored at our temperatures. A homogeneous reaction would have to have an activation energy of not more than 8 kcal/mole in order that it occur in our system. This, of course, is not unreasonable in view of the rapidity of attainment of the room-temperature equilibrium, but it must be considered speculative at the moment.

We note that alkyl nitrites may also decompose through a favorable six-center elimination of HNO_2 with a fairly low activation energy (perhaps only 40 kcal/mole less 5 kcal/mole ring strain), 35 kcal/mole. Evidently they do not decompose this way and we infer from the observed[15] Arrhenius parameters, $A = 10^{14.5}$ sec^{-1} and $E = 38$ kcal/mole, that it is the low A factor of the HNO_2 elimination process (say 10^{11} sec^{-1}) compared with the high A factor for the competing NO elimination which plays the decisive role in governing the path of the reaction.

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Chemical Ionization Mass Spectrometry. VII. Reactions of Benzene Ions with Benzene[1a]

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Abstract: In the electron impact mass spectrum of benzene measured at pressures between 1 and 1000 μ, the predominant $C_6H_6^+$ ion does not react rapidly with benzene. Ionization of benzene by electron transfer to rare gas ions under chemical ionization conditions produces widely differing fragmentation patterns and thus permits clear-cut studies of specific fragment ions. Ionizing benzene with Xe^+ gives 94% $C_6H_6^+$ which again does not react rapidly with benzene. Using Ar^+, 14% $C_3H_3^+$, 30% $C_4H_4^+$, and 16% $C_6H_5^+$ are produced. Benzene does not react with $C_3H_3^+$; it electron transfers to $C_4H_4^+$, and both electron transfers to and condenses with $C_6H_5^+$ to give $C_6H_6^+$ and $C_{12}H_{11}^+$. Electron transfer from benzene to Ne^+ gives 37% $C_4H_3^+$ which can take an electron from benzene. Since $C_6H_6^+$ is unreactive and readily formed by electron transfer to benzene fragment ions, the radiation chemistry of benzene must be due mainly to free radicals.

To aid the understanding of the radiolysis and other high-energy chemistry of benzene, we have made positive ions from this aromatic hydrocarbon and studied their reactions with benzene molecules at pressures between 1 and 1000 μ. Barker[2a] and Hamill[2b] have briefly looked at secondary ions in a mass spectrometer containing benzene but only at pressures below 2 μ.

In our study, positive ions were made from benzene by both electron impact and electron transfer to rare gas ions. Ion production by electron transfer has received much study but mainly in double mass spectrometers.[3] High-pressure mass spectrometer studies have been done, however, on electron transfer from ethylene to rare gas ions.[4]

Experimental Section

The Esso chemical physics mass spectrometer, which has been described elsewhere,[5] was used for this work. A determination of the ionic intensities as a function of source pressure at 210° was made for pure benzene using a previously described technique.[6] Ionization of benzene by electron transfer to rare gas ions was effected using chemical ionization techniques also described elsewhere.[5] Since chemical ionization experiments with methane at 170° were being done concurrently with the rare gas work, this lower temperature was used in the electron-transfer experiments.

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