the fairly symmetrical structure. Similarly, cyclohexyl bromide has critical wave length values only 20 to 35% larger than those of n-hexyl bromide,[8] although its viscosity is more than twice as large.[9] A similar trend is evident in the four isomeric butyl bromides, which show an increase in viscosity[9] and a decrease in critical wave length[9] as the molecule changes from more or less linear to nearly spherical in form.

Although the molar volume of acetophenone, 117 cc. at 20°, is not much larger than that of cyclohexanone, 103 at 20°, and the viscosity is somewhat lower, the critical wave length and its ratio to viscosity are much larger. The greater difficulty of dipole orientation thus indicated may be attributed to the considerable protrusion of the CH_3CO group from the ring. In comparison with acetophenone, the critical wave length of 2-acetonaphthone is unexpectedly high, although the large naphthyl group should increase both critical wave length and viscosity. The molar volume of 2-acetonaphthone is about 30% higher, while the ratios of the critical wave length to the viscosity are almost twice as large. For 1-chloronaphthalene which is somewhat similar in shape and slightly smaller, the critical wave length[8] to viscosity[9] ratio is 3.7 at 1° and 3.3 at 55°. The molar volume of benzophenone, 170 cc. at 60°, is slightly larger than that of 2-acetonaphthone, 158, and the viscosity is nearly the same, but the critical wave length and its ratio to viscosity are much smaller, although they might be expected to be about the same. The ratio of the critical wave length to the viscosity is smaller for benzophenone than for acetophenone in spite of the larger size of the molecule. It would appear that, among these ketones, the behavior of 2-acetonaphthone is distinctly anomalous. It is evident that, as frequently observed before, marked changes in molecular shape cause marked irregularities in the relations between molecular volume, critical wave length and viscosity, but the relationships observed are consistent in order of magnitude.

The critical wave lengths found for phenyl ether are consistent with the value 0.53 cm. calculated from Fischer's relaxation time[3] determined by a thermal method in dilute benzene solution at 23°, which gives 0.85 for the ratio of critical wave length to viscosity. The phenyl ether molecule is very similar in size and shape to that of benzophenone, the molar volumes being 164 and 170 cc., respectively, at 60°. It is, therefore, surprising to find the critical wave lengths of phenyl ether only about one tenth and the ratios of critical wave length to viscosity only about one seventh of those for benzophenone. Fischer suggested that the low value for phenyl ether might be due to orientation by internal motion of the molecule, in particular, of the oxygen atom, which might occur in the other ethers as well. There appears, however, to be nothing markedly anomalous in the critical wave lengths found for ethyl ether,[2] 0.45 cm. at 20°, 0.90 cm. for butyl ether in dilute benzene solution,[3] and 6.5 cm. for decyl ether.[2] Also the values of the critical wave length to viscosity ratio are, for the pure liquid, half as large as those of cyclohexanone and, for the benzene solution, about the same size. Interpretation of the results for phenyl ether must wait upon the results of other measurements upon related substances.

PRINCETON, NEW JERSEY

Reactions of Nitrate Esters. IV. Kinetics of Hydrazinolysis[1]

BY RAYMOND T. MERROW

In homogeneous systems, both the S_{NC} and S_{NX} type reactions of nitrate esters with hydrazine are first order with respect to the esters. The former is also first order in hydrazine, and solvent effects point to molecular hydrazine as the reactive nucleophile. The rate data for reduction (S_{NX}) indicate an apparently high order dependence on hydrazine concentration. Solvent effects suggest that $N_2H_3^-$ may be involved in the rate-determining step. Activation energies have been calculated for both processes. A heterogeneous reduction gives apparent zero-order kinetics, and there is evidence that diffusion of one reactant into the other is the rate-controlling process.

The hydrazinolysis of primary and secondary nitrate esters has been shown[2] to involve two major processes. Concentrated hydrazine solutions mainly effect a reduction of alkyl nitrates, via an initial displacement at nitrogen[3] (S_{NX} process),[4] resulting in the formation of nitrite ion, nitrogen, nitrous oxide, ammonia, hydrazoic acid and the

(1) Presented before the 128th National Meeting of the American Chemical Society, Minneapolis, Minn., September 1955.

(2) R. T. Merrow and R. W. Van Dolah, THIS JOURNAL, 76, 4522 (1954).

(3) R. T. Merrow and R. W. Van Dolah, ibid., 77, 756 (1955).

(4) M. Anbar, I. Dostrovsky, D. Samuel and A. D. Yoffe, J. Chem. Soc., 3603 (1954). The symbol S_{NC} is used to denote nucleophilic attack on the α-carbon atom of the alkyl group, and S_{NX} for nucleophilic attack on the central atom X of the oxy-acid (e.g., X = N in nitrate or nitrite esters).

alcohol corresponding to the ester. A displacement on carbon (S_{NC}),[4] yielding nitrate ion and substituted hydrazines, occurs to an increasing extent as more dilute hydrazine solutions are used. Aralkyl nitrates undergo this latter process predominantly in both concentrated and dilute hydrazine.[2]

A kinetic study of the two processes has been carried out in an attempt to ascertain whether differences in mechanism, other than the locus of attack, exist.

With alkyl nitrates, considerable reduction always occurs, even in dilute hydrazine solutions, and it has not been possible to isolate the S_{NC} reaction of these esters. With benzyl nitrate, on the other hand, the S_{NC} reaction occurs to the extent of more

than 95% in dilute hydrazine, and this reaction can be followed alkalimetrically. The stoichiometry is one mole of base consumed per mole of nitrate ester, and the kinetics are second order (first order in each reactant). A slow, apparently autocatalytic decline in base concentration, which was observed in dilute solutions of hydrazine alone, occurred only to a negligible degree during the time required for nearly complete hydrazinolysis of the ester, as indicated in Fig. 1.
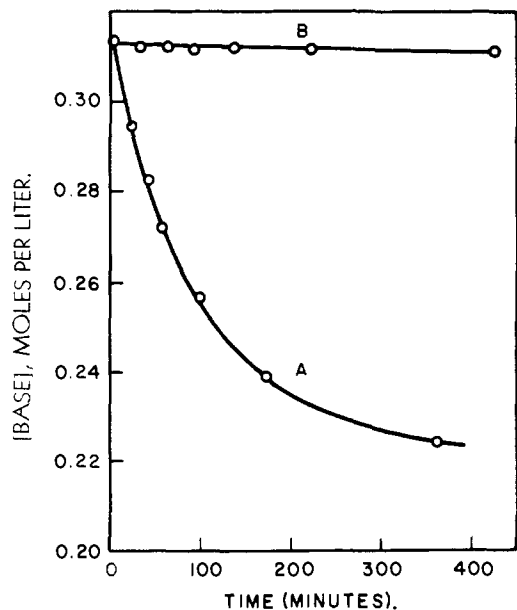

Fig. 1.—Consumption of base in hydrazinolysis of benzyl nitrate (curve A) and in autodecomposition of hydrazine (curve B) in 60% ethanol at 52°.

The rate data for the benzyl nitrate reaction are given in Table I. In the temperature range at which this study was made, the rate constants were found to be lower in 90% than in 60% ethanol,[5] while the activation energy was essentially the same in both solvents. A single rate run in 60%

TABLE I

HYDRAZINOLYSIS OF BENZYL NITRATE IN AQUEOUS ETHANOL

N₂H₄, M	RONO₂, M	Alcohol (vol. %)	Temp., °C.	10⁴k (l./mole/ sec.)	E, (kcal./mole)	log A
0.336	0.171	60	52.17	5.66		
.312	.094	60	52.17	5.53		
.294	.107	60	39.95	1.80	18.1 ± 0.5	8.93
.293	.143	60	39.95	1.75		
.294	.090	60	28.96	0.69		
.290	.066	60	28.96	0.61		
.298	.101	90	52.17	3.07		
.307	.117	90	39.95	1.04	17.3 ± 0.4	8.08
.192	.100	90	28.96	0.39		
.325	.098	60ᵃ	28.96	0.50		
.294	.142	60ᵇ	52.17	3.50		

ᵃ 0.1 M in LiCl.   ᵇ 1-Propanol used instead of ethanol.

(5) All solvent compositions are expressed in volume per cent., based on volumes before mixing. The required amounts of water (if any) and hydrazine were measured, and mixtures were made up to volume, after addition of the nitrate esters, with the ethanol or other organic solvent.

propanol also gave a smaller value for k than corresponding runs in 60% ethanol.

The effect of solvent on rate is in accord with the Hughes–Ingold theory[6] of solvent effects for an S_N2 reaction between two uncharged molecules. Cristol and Barasch,[7] however, have called attention to the non-validity of the use of relative rate constants alone in comparing solvent effects, and have recommended consideration of activation energies as better, but not infallible, criteria. In the present work, no conclusions can be drawn from activation energies, since the values obtained in different solvents were the same within experimental error. Baker and Easty[8] reported a similar solvent effect on the rate of neutral hydrolysis of alkyl nitrates, with no change in activation energy. That reaction has been shown[9] to proceed predominantly by an S_{NC} mechanism. On the basis of these similarities, and the fact that the data fit a second-order rate law and give reasonable values for E and A, it is concluded that molecular hydrazine is the nucleophile involved in the S_{NC} process.

In all of the runs for which data are recorded in Table I, hydrazine was present in two- or threefold excess. With benzyl nitrate in excess, treatment of the data for a second-order rate law did not yield a straight line, but a curve of increasing slope. This effect is probably due to the increasing importance of consecutive reactions leading to polyalkylated hydrazine derivatives. Some typical treatments of data are shown in Fig. 2.
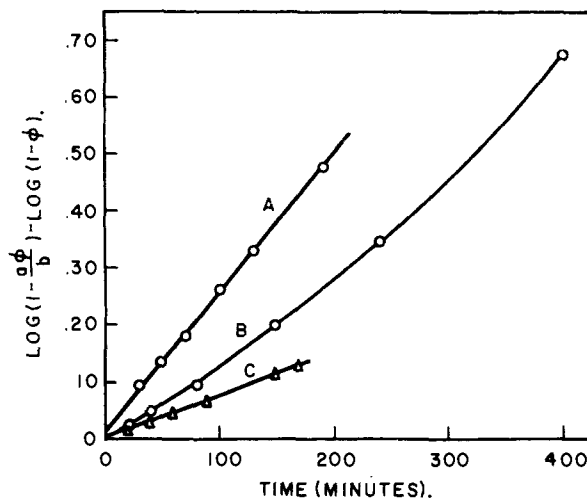

Fig. 2.—Treatment of data according to second-order rate law with hydrazine in excess (1.96:1, curve A) and with benzyl nitrate in excess (1.97:1, curve B; 1.58:1, curve C); solvent, 60% ethanol; temperature, 52°.

The reduction of primary and secondary alkyl nitrates by means of concentrated hydrazine was conveniently studied by measuring the pressure of the evolved gases. The validity of the method was established in two ways: (1) for a given hy-

(6) E. D. Hughes and C. K. Ingold, J. Chem. Soc., 244 (1935).
(7) S. J. Cristol and W. Barasch, THIS JOURNAL, 74, 1658 (1952).
(8) J. W. Baker and D. M. Easty, J. Chem. Soc., 1193 (1952).
(9) S. J. Cristol, B. Franzus and A. Shadan, THIS JOURNAL, 77, 2512 (1955).

drazine concentration, the total pressure rise during a run was shown to be directly proportional to the amount of nitrate ester used; (2) the same rate constants were obtained from polarographic measurements of nitrate ester concentration as from the manometric method. The reduction was carried out in both homogeneous and heterogeneous systems.

The homogeneous reaction, in which a small amount of nitrate ester was dissolved in a mixture of hydrazine and an organic solvent, was shown to be first order in nitrate ester concentration. The order with respect to hydrazine could not be established with any degree of certainty because of the apparent complexity of the mechanism (see below). For example, a series of runs with ethyl nitrate in 25, 50 and 75% ethanolic hydrazine at 27° gave rate constants of 3.27×10^{-5}, 48.0×10^{-5} and 282×10^{-5} sec.$^{-1}$, respectively. If the effect were considered to be due entirely to changing the concentration of a reactant, and medium effects were discounted, the order in hydrazine would appear to be approximately 4.

Pseudo-first-order rate constants and activation energies were measured for the hydrazinolysis of ethyl, n-butyl and 2-octyl nitrates in 50% ethanolic hydrazine, using the anhydrous base. Replacement of half of the ethanol by water in a series of runs with butyl nitrate resulted in an increase in activation energy, and a decrease in the rate constants over the range of temperatures studied. These results are shown in Table II. When 95% hydrazine was substituted for the anhydrous base in a series of runs with ethyl nitrate, the rate constants were lower, but the activation energy was essentially unchanged (Table III). Replacement of half of the ethanol by water again resulted in a lowering of the rate constants and in an increase in activation energy. While activation energies were obtained in only the two solvent systems (hydrazine–ethanol and hydrazine–ethanol–water), rate constants were measured at a single temperature in a number of others. In general, as indicated in Table IV, the rates were greater in the less highly ionizing solvents.

TABLE II

RATE DATA FOR HYDRAZINOLYSIS OF ALKYL NITRATES IN 50% ETHANOLIC HYDRAZINE

Nitrate	Temp., °C.	$10^4 k$ (sec.$^{-1}$)	E (kcal./mole)
Ethyl	28.96	6.72, 5.89	
	39.95	10.1, 10.2, 11.9	
	52.17	26.7, 23.1, 30.7	12.4 ± 1.1
n-Butyl	28.96	4.15, 3.75, 3.92[a]	
	39.95	7.23, 7.63, 6.98[a]	
	52.17	14.7, 14.7	11.0 ± 0.3
	28.96	2.09,[b] 2.01[b]	
	39.95	4.69,[b] 4.40[b]	
	52.17	11.4,[b] 12.3[b]	14.8 ± 0.4[b]
2-Octyl	28.96	0.88	
	39.95	1.82	
	52.17	4.12	13.0 ± 0.3

[a] These rate constants were determined polarographically. All others were obtained by manometry. [b] Solvent for these runs contained 25% water. All others were anhydrous.

TABLE III

HYDRAZINOLYSIS OF ETHYL NITRATE IN 50% HYDRAZINE[a] IN AQUEOUS ETHANOL

Temp., °C.	Total % H_2O in solvent	$10^4 k$ (sec.$^{-1}$)	E(kcal./mole)
28.96	2.5	3.95	
39.95	2.5	8.07	11.9 ± 0.2
52.17	2.5	16.33	
28.96	27.5	2.87	
39.95	27.5	5.83	13.8 ± 0.9
52.17	27.5	14.67	

[a] Commercial 95% hydrazine constituted 50% of the total volume.

TABLE IV

RATES OF REACTION OF ETHYL NITRATE IN 50% HYDRAZINE[a] AT 27.03°

Remainder of solvent	$10^4 k$ (sec.$^{-1}$)	Remainder of solvent	$10^4 k$ (sec.$^{-1}$)
CH_3OH	3.25	$n\text{-}C_4H_9OH$	5.22
C_2H_5OH	4.80	CH_3CN	4.69
$n\text{-}C_3H_7OH$	5.57	$C_2H_5OH\text{—}H_2O(1:1)$	3.27

[a] Commercial 95% hydrazine.

The lower rate constants and higher activation energy in the more highly ionizing solvent (hydrazine–ethanol–water) are in agreement with the predictions of the Hughes–Ingold theory[6] for a reaction of an ion with a neutral molecule. The relative rates are, of course, dependent upon the temperature range of the investigation[7] and, in the present instance, extrapolation indicates that, at higher temperatures, the rate would be higher in the more polar solvent. The rates of alkaline hydrolysis of methyl and ethyl nitrate are lowered by increasing the polarity of the solvent,[8] while changes in activation energy with solvent are small and in opposite directions for the two esters.

There appears to be no doubt that this reduction involves attack by a nucleophilic species. No gas evolution was observed when solutions of hydrazinium salts were used instead of the free base. Further, under conditions where the reaction does proceed, it was found that addition of alkali increased the rate, while addition of acid (in sufficient amount to affect measurably the pH) had a retarding effect.

The fact that the activation energy of reductive hydrazinolysis was found to be larger in the more polar solvent, is suggestive of an ion, $N_2H_3^-$, perhaps as the nucleophilic reagent responsible for the reduction process. This would certainly parallel the reactions of nitrate esters with water and with hydroxyl ion, in which the uncharged molecule (H_2O) attacks mainly at carbon,[9] while the anion (OH^-) attacks predominantly at the nitrogen atom.[4,9] Participation of the similar ions NH_2^- and RNH^- in ammonolysis[10] and aminolysis[11] of certain carboxylate esters has been suggested on the basis of kinetic studies.

In the absence of any reactant, the concentration of hydrazide ion is very small; Pleskov[12] gives a value of 2×10^{-25} for the ion product for auto-

(10) R. L. Betts and L. P. Hammett, THIS JOURNAL, 59, 1568 (1937).
(11) P. J. Hawkins and I. Piscalnikow, ibid., 77, 2771 (1955).
(12) V. A. Pleskov, Acta Physicochim. (U.S.S.R.), 13, 662 (1940); C. A., 36, 2214 (1942). It is assumed that ion concentrations are expressed in moles per liter.

protolysis of anhydrous hydrazine. This corresponds to a concentration of about 4×10^{-13} M for hydrazide ion. A simple second-order rate expression involving hydrazide anion and nitrate ester would therefore require a very high value for the pre-exponential (A) factor. For example, the A factor calculated from the rate data for 2-octyl nitrate given in Table II (using the above value for $[N_2H_3]$) is approximately 10^{21} l./mole/sec.
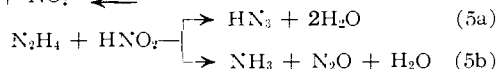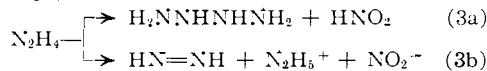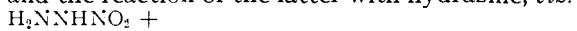
However, the concentration of hydrazide ion in these reaction mixtures may be considerably greater than the autoprotolysis constant would indicate, if the equilibrium (1) is displaced by removal of hydrazinium ion through rapid reactions, for example, with nitrite ion.

$$2N_2H_4 \rightleftharpoons N_2H_5^+ + N_2H_3^- \qquad (1)$$
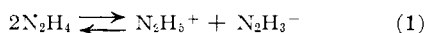
Electroneutrality could be maintained by replacement of this cation by the ammonium ion, produced by equilibration of ammonia (formed in (4) or (5b) below) with nitrous acid or with hydrazinium ion itself. On the basis of the observed kinetic solvent effects, it is suggested that the rate-controlling step may be

$$RONO_2 + N_2H_3^- \longrightarrow RO^- + H_2NNHNO_2 \qquad (2)$$
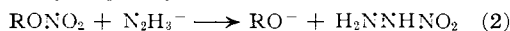
but that the rate expression is complicated by other processes which affect the concentration of $N_2H_3^-$ through their effect on $N_2H_5^+$. Subsequent steps of the previously suggested mechanism[2] include the formation of hydrazoic and nitrous acids, and the reaction of the latter with hydrazine, viz.

$$H_2NNHNO_2 +$$

$$N_2H_4 \text{---} \begin{cases} \longrightarrow H_2NNHNHNH_2 + HNO_2 & (3a) \\ \longrightarrow HN{=}NH + N_2H_5^+ + NO_2^- & (3b) \end{cases}$$

$$2HN{=}NH \longrightarrow HN{=}NNHNH_2 \longrightarrow HN_3 + NH_3 \qquad (4)$$

$$N_2H_5^+ + NO_2^- \rightleftharpoons$$

$$N_2H_4 + HNO_2 \text{---} \begin{cases} \longrightarrow HN_3 + 2H_2O & (5a) \\ \longrightarrow NH_3 + N_2O + H_2O & (5b) \end{cases}$$

In addition, the concentration of hydrazinium ion, and, hence, that of hydrazide ion, is influenced by the following acid–base equilibria

$$N_2H_4 + HN_3 \rightleftharpoons N_2H_5^+ + N_3^-$$

$$N_2H_4 + H_2O(ROH) \rightleftharpoons N_2H_5^+ + OH^-(RO^-)$$
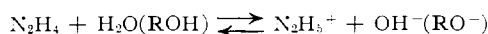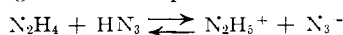
It would not be surprising, therefore, to find a non-simple relationship between hydrazine concentration and the rate of a reaction dependent on $N_2H_3^-$.

A few rate experiments have been run on the heterogeneous reaction of butyl nitrate with excess hydrazine in the absence of added solvent. The rate of pressure change was constant for any given run, indicating a zero-order reaction. In the absence of stirring, the rate was found to vary with the amount of butyl nitrate, but was essentially independent of the volume of hydrazine used, which suggests that the rate-controlling factor may be the interfacial area between the butyl nitrate droplets and the hydrazine.

Only a limited amount of qualitative information is available regarding effects of ionic strength on rates. No primary salt effect is to be expected, of course, since one of the reactants (the nitrate ester) is a neutral molecule. A small decrease in the rate of the benzyl nitrate reaction was noted on

addition of LiCl to the mixture. The rate of hydrazinolysis of butyl nitrate in hydrazine–ethanol–water was increased by the addition of LiCl, NaOH or HCl, provided in the latter case that the concentration of HCl was small in relation to the hydrazine concentration. This rate increase is probably due to a secondary salt effect on the degree of ionization (autoprotolysis) of hydrazine, and thus lends support to the postulate that the hydrazide ion is the active species in this reaction.[13] As noted above, larger amounts of acid caused a decrease in rate, probably by reducing the concentration of $N_2H_3^-$ and increasing that of $N_2H_5^+$.

Experimental

Analytical Procedures.—In studying the hydrazinolysis of benzyl nitrate under second-order conditions (dilute hydrazine solutions), the extent of reaction was determined by alkalimetric titration. Aliquots containing from 0.5 to 2.0 milliequivalents of base were withdrawn and run into 15 ml. of water and the solutions were titrated with standard 0.5 N HCl. Brom cresol green (4 drops) was used as the indicator, and the end-point was taken as the point where the color matched that of 20 ml. of pH 4.0 buffer solution containing four drops of the indicator.

Most of the runs in concentrated hydrazine solution were followed manometrically. The reaction mixtures were made up in volumetric flasks at the reaction temperature and immediately transferred to the thermostatted reaction vessel, a ground-glass stoppered erlenmeyer flask connected by a sidearm to a gas bulb and manometer. The flask was stoppered, and gas pressure was measured periodically. No agitation was used in the heterogeneous reactions. The nitrate ester was pipetted into the hydrazine, and remained as droplets at the bottom of the reaction flask, diminishing in size until the mixture was completely homogeneous at the end of the reaction.

In a few runs of this sort, nitrate ester concentration was followed polarographically by the method of Whitnack, et al.[16]

Calculation of Rate Data.—Second-order rate constants for the benzyl nitrate hydrazinolyses were determined graphically. The following form of the equation for a second-order rate law was used

$$\frac{d}{dt}\left(\log \frac{1 - a\phi/b}{1 - \phi}\right) = \frac{(b - a)k}{2.303}$$

where b = initial concentration of component in excess; a = initial concentration of other component; and ϕ = fraction of reaction at time t.

Pseudo-first-order rate constants were obtained from the manometric data, by plotting $\log (P_\infty - P_t)$ vs. time and multiplying the slope of the line by 2.303. Where nitrate ester concentration was followed, $\log [RONO_2]$ was plotted.

In the heterogeneous runs, the pressure of the gaseous products increased linearly with time (indicating zero-order kinetics), and the slopes of these lines gave a direct measure of the rate.

Activation energies were calculated in the usual manner.

CHINA LAKE, CALIFORNIA

(13) The author is indebted to a referee for this suggestion.

(14) G. R. Lucas and L. P. Hammett, THIS JOURNAL, **64**, 1928 (1942).

(15) R. L. Shriner and E. A. Parker, ibid., **55**, 766 (1933).

(16) G. C. Whitnack, J. M. Nielsen and E. S. C. Gantz, ibid., **76**, 4711 (1954).