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Kinetics of Thermal Decomposition of *o*-Nitrophenyl Azide

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The rate of thermal decomposition of *o*-nitrophenyl azide into benzofuroxan and nitrogen has been measured for the pure liquid azide and for solutions of azide in di-*n*-butyl phthalate, cyclohexanol, *n*-heptane and mixtures of heptane and cyclohexanol over a temperature range of 65 to 90°. The first-order rate constants were found to be $k = 2.7 \times 10^{12} \exp(-26{,}300/RT)$, $2.4 \times 10^{12} \exp(-26{,}300/RT)$ and $3.4 \times 10^{12} \exp(-26{,}600/RT)$ in the di-*n*-butyl phthalate, cyclohexanol and heptane solutions, respectively. In the pure liquid state $k = 6.2 \times 10^{12} \exp(-26{,}600/RT)$. The entropies of activation were found to be -3.9 ± 0.6 e.u. in dibutyl phthalate, -3.7 ± 0.7 e.u. in cyclohexanol, -3.5 ± 0.5 e.u. in heptane and -2.2 ± 0.4 e.u. in the pure liquid state.

Introduction

In the course of study of the physical and thermodynamic properties of organic azides and some related compounds[1] in this Laboratory, it was of interest to study the kinetics of the thermal decomposition of *o*-nitrophenyl azide to form benzofuroxan, one of the so-called meso-ionic compounds. The extensive studies of the thermal decomposition of benzazide by Newman, Lee and Garrett[2] and the study of the decomposition of phenyl azide by Russell[3] lent further interest to this study. The rates in dibutyl phthalate and in the pure liquid state were followed by measuring the volume of mercury displaced by the evolved nitrogen at constant pressure; the rates in cyclohexanol and heptane were followed spectrophotometrically.

Experimental

Reagents. (**a**).—The *o*-nitrophenyl azide was prepared according to the method of Boyer and Smith[4] by treating diazotized *o*-nitroaniline with sodium azide. The *o*-nitroaniline, a "practical grade" product supplied by Eastman Organic Chemicals Co., was recrystallized from ethanol before use in the preparation of the azide. The prepared azide was purified by several recrystallizations from 95% ethanol and stored at 0°. The azide was quite stable against decomposition at this temperature, but it was, nevertheless, recrystallized periodically during the course of this work. The melting point recorded by a total-immersion Anschütz thermometer was 51.6–51.8° (literature 51–53°).

(**b**).—The benzofuroxan was prepared by refluxing the azide in toluene for about an hour; the toluene was then removed by passing an air stream over the solution. The pale yellow furoxan crystals were then recrystallized several times from ethanol–water solution to give a product melting at 69.2–69.5°.

(**c**) **Solvents.**—The di-*n*-butyl phthalate (ester of 1,2-phthalic acid) was an Eastman Organic Chemicals Reagent grade material; it was used without further purification. The cyclohexanol and heptane were obtained from the Matheson, Coleman and Bell Division of the Matheson Company. Drying and fractional distillation of these failed to change the absorption characteristics; further, the rates of decomposition of the azide were not altered by further purification of these solvents; in subsequent work they were used without further purification.

Apparatus.—The constant temperature oil-bath (Precision Scientific Company No. 66548) was heated by means of three 125 watt knife heaters, each individually controlled by means of "Variacs." The operation of one of the heaters was governed by a "merc-to-merc thermoregulator" (Precision Scientific Company No. M41013), while the two remaining heaters heated the bath constantly. By changing the input voltage to the heater, while maintaining efficient stirring, it was possible to regulate the bath temperature to ±0.015°.

The thermometers used were marked in tenths of a degree; their accuracy was determined by calibration against a platinum resistance thermometer with a Bureau of Standards certificate.

For the decomposition of the pure liquid azide and solutions in di-*n*-butyl phthalate, the rates were followed by measuring the volume of mercury displaced by the evolved nitrogen, at constant pressure and temperature. A 250-ml. three-neck flask with standard taper ground-joint connections served as the reaction chamber. Since dibutyl phthalate solutions readily became supersaturated with nitrogen a high-speed stirrer powered by a geared-drive, rheostat-controlled electric motor of $^{1}/_{18}$ h.p. (Arthur S. La Pine and Co. No. 382–66) was used to obviate this difficulty. The reaction chamber was connected to the mercury reservoir with glass-to-glass tubes supported by neoprene tubing. To the mercury reservoir was attached a manometer, filled with nitrogen-saturated dibutyl phthalate; the manometer was placed close to the reservoir so that it could be entirely immersed in the oil-bath. A connection between the reservoir and the burets was similarly constructed of glass tubing, supported by Tygon tubing; a two-way stopcock linked the connecting tube to the burets. The burets were calibrated by weighing the water delivered from them. An air reservoir, connected to the other side of the manometer acted as a buffer, eliminating difficulties due to barometric fluctuations during a kinetic run. The entire apparatus, reaction flask, reservoir, manometer and buffer flask were completely immersed in the oil-bath, and flushed with nitrogen before kinetic measurement was made.

The kinetics of the decomposition in the solvents heptane, cyclohexanol and mixtures of these were followed spectrophotometrically using a Beckman DU spectrophotometer.

The dielectric constants of the heptane–cyclohexanol mixtures were measured with a conventional heterodyne-beat apparatus.[5]

Procedure and Analysis of Data.—A preliminary study of the reaction, using a Warburg apparatus, showed that the decomposition went to completion; the loss in weight of the sample agreed with the pressure developed in the apparatus. The Warburg apparatus was then discarded for the above-described apparatus in order to gain higher precision. In the spectrophotometric studies, a calculation of the concentrations of both azide and product (benzofuroxan) from absorbancy measurements and previously determined Beer's law equations for the separate components, indicated that the sum of the reactant and product was throughout the kinetic run equal to the quantity of azide originally introduced. This showed that no side-reaction of any sort was occurring.

In the gasometric analysis, as the *o*-nitrophenyl azide either in the pure liquid state or in a nitrogen-saturated solution of dibutyl phthalate, decomposed to benzofuroxan, nitrogen gas evolution caused an increase in pressure, recorded by the di-butyl phthalate manometer. Mercury was then allowed to flow out of the reaction system into the buret until the pressure was again equalized. The system was

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[1] (a) T. F. Fagley, J. F. Albrecht, Jr., and E. Klein, THIS JOURNAL, **75**, 3104 (1953); (b) T. F. Fagley and H. W. Myers, *ibid.*, **76**, 6001 (1954); (c) T. F. Fagley, Thermochemical Bulletin No. 2, Mar., 1956 (Sub-Commission on Experimental Thermochemistry of the International Union of Pure and Applied Chemistry).

[2] M. S. Newman, S. H. Lee and H. B. Garrett, THIS JOURNAL, **69**, 113 (1947).

[3] K. E. Russell, *ibid.*, **77**, 3487 (1955).

[4] P. A. S. Smith and J. H. Boyer, *Org. Syntheses*, **31**, 14 (1951).

[5] We are indebted to Dr. J. M. Scott for the use of the dielectric constant apparatus.

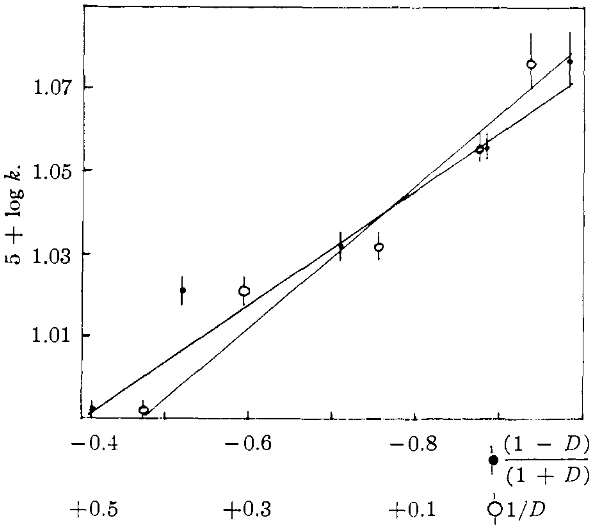

Fig. 1.—Plot of log *k* *versus* functions of dielectric constant, *D*, of solvent; $t = 78.52°$.

brought to pressure equilibrium at equal time intervals and the volume of mercury recorded *versus* time.

The Guggenheim method[6] was used in evaluating the reaction rate constant *k* in order to avoid inaccuracy and inconvenience of using the V_∞ reading. Rather than plotting a graph for each run, the method of least squares was employed. Since the time interval was known quite precisely, all significant error was assumed to reside in the volume measurements.

In the studies of heptane and cyclohexanol solutions of the azide a different technique was necessary because of the high volatility of heptane and viscosity of cyclohexanol.

(a) About 500 g. of cyclohexanol was weighed into a three-necked flask, fitted with a motor-driven stirrer and a condenser. The solvent was allowed to equilibrate thermally overnight. When a run was made, a weighed amount of azide was added to the solvent. Weighings were made on a micro-balance. At regular time intervals samples were withdrawn from the flask and transferred to tubes immersed in an ice-bath. The transfer was effected by means of a 10-ml. serological pipet fitted to a hypodermic syringe by a rubber coupling. The tip of the pipet was broken off to increase the speed of transfer. The reaction was effectively stopped the moment the solution reached the chilled tube, since the decomposition does not proceed rapidly below 50°. Total transfer time from flask to tube amounted to four seconds; and completion of transfer was made to coincide with a minute on the stopwatch. The absorptions of the samples were determined, with pure solvent as the reference.

(b) In the heptane studies, solutions of azide were placed in 10-ml. thin-walled glass ampoules which were then cooled in an ice-bath and sealed to prevent evaporation. These were placed in the bath in a small wire basket. At regular time intervals an ampoule was withdrawn from the bath and plunged into an ice-water bath. Transfer time in this case was about one second. At the conclusion of the run, the ampoules were broken open and the absorption of each solution measured, with pure heptane as reference.

(c) It was found that *o*-nitrophenyl azide exhibited absorption maxima at 240 and 320 mμ in cyclohexanol, with a shoulder appearing at 255 mμ. Benzofuroxan showed a single absorption peak at 360 mμ in the range from 235 to 400 mμ. Because of the strong solvent absorption below 240 mμ, the maximum at 240 mμ could not be used, although the shoulder occurring at 255 for the azide yielded good Beer's law curves; therefore analysis was made at 255 mμ for the azide and at 355 mμ for the benzofuroxan when the solvent was cyclohexanol. For heptane solutions the 320 mμ peak was used for the azide and the 360 mμ for the benzofuroxan. Serial dilutions, using pipets calibrated with pure heptane, of a stock solution of azide in heptane were made and their absorptions measured. In the case of the viscous cyclohexanol solutions, solutions were made up by weight and Beer's law curves determined. Similar curves were obtained for the solutions of benzofuroxan. Four equations were obtained from the values obtained spectrophotometrically and the known concentrations of the solutes. Rather than obtain the absorbancy indices (extinction coefficients) graphically, the method of least squares was used to obtain equations of the form

$$A_{255} = E_1C_A + b_1 \quad (1)$$
$$F_{355} = E_2C_F + b_2 \quad (2)$$
$$A_{255} = E_3C_A + b_3 \quad (3)$$
$$F_{355} = E_4C_A + b_4 \quad (4)$$

where

A is the optical density, or absorbancy, for pure azide in soln. at the wave length specified
F is the corresponding value for the benzofuroxan
E is the extinction coefficient, or absorbancy index, for the compd. at each particular wave length
C_A is the concn. of the azide
C_F is the corresponding value for the benzofuroxan; and
b is the calcd. intercept for the Beer's law curve.

(The empirical intercepts were retained in the final expression rather than adjusting the equations to make $b = 0$.)

Since the extinctions are additive at a given wave length, equations 1 and 2 were added as were equations 3 and 4, giving two equations each of which related both the concentration of the azide and the concentration of the benzofuroxan to the measured optical density. The cells used in this investigation were 1 cm. silica cells obtained from Beckman Instruments, Inc. They were calibrated for each solvent system at the two wave lengths by reading them against one cell containing pure solvent. This was repeated each time a Beer's law equation was determined. The small corrections were used to obtain the true optical density values.

The combined Beer's law equations are

for the solvent cyclohexanol

$$D_{255} = 7951C_A + 695.4C_F - 0.028$$
$$D_{355} = 1203C_A + 6681C_F - 0.0004$$

and for the solvent heptane

$$D_{320} = 2534C_A + 1512C_F + 0.018$$
$$D_{360} = 420.9C_A + 7101C_F + 0.007$$

where *D* is the optical density observed for a mixture of azide and benzofuroxan in solvent at the wave length specified. As a further test of the reliability of the Beer's law equations known mixtures of azide and furoxan were made up in the solvents and their absorptions measured. The agreement between the concentrations calculated from the equations and the concentrations calculated from the weights of azide and furoxan was about one per cent., the limit of precision of the instrument for these dilute solutions.

For studies in the mixed solvent system (heptane–cyclohexanol) the solvents were weighed into a volumetric flask which was filled to the mark; from the known densities of the pure solvents and measured densities of the mixtures, both the volume fraction and the mole-fraction of the constituents were calculated. Solutions of the azide in these mixed solvents of known composition were then studied kinetically.

The determination of the order of the reaction was made graphically. Various plots of a function of the azide concentration *versus* time indicated that the reaction was definitely first order. Furthermore, the fact that the rate constants obtained by two methods, from the concentration of decomposing azide and from the concentration of benzofuroxan formed, were identical, within the limits of precision of the experiments, and the fact that the sum of the azide and benzofuroxan concentrations was a constant throughout a kinetic run showed that the reaction proceeded without any complicating side reactions.

Rather than plot curves each time a run was completed, the data both in the gasometric and in the spectrophotometric work were treated analytically by the method of least squares, all experimental concentrations being used. For the constants evaluated in the gas-evolution technique, the Guggenheim method did not require knowledge of either V_0 or V_∞. The evaluation of the *k*'s from the azide concentration in the heptane and cyclohexanol solutions also did not

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[6] E. A. Guggenheim, *Phil. Mag.*, **2**, 538 (1926).

require knowledge of the initial concentration, a_0, of azide. However, to calculate k from changes in the furoxan concentration with time, the rate expression d(furoxan)/dt = k(azide) = $k(a_0 - x)$, where x is the concentration of furoxan at time t, required that the concentration of azide at the time the ampoules reached constant temperature be known. For the cyclohexanol solution studies, a_0 was simply that calculated from the weight of azide introduced into the flask containing the thermally equilibrated solvent at t, taken as $t = 0$. For the heptane solutions in the ampoules, the time lag involved in attainment of constant temperature necessitated a different method. A linear plot of log(azide) *versus* time was extrapolated to zero time (in this case, time of immersion); from this intercept the effective concentration of azide at temperature equilibrium was found. This quantity less the concentration of furoxan at any time t (measured from time of immersion) was used as the measure of $(a_0 - x)$. The k's so calculated agreed with those evaluated from the azide concentrations measured spectrophotometrically with time. At the highest temperature at which the rates in heptane were measured this extrapolation proved unsatisfactory. The following method was used: at some time, t, after thermal equilibrium had been established (about 10 minutes was required; this first ampoule being withdrawn at, say, 20 minutes) both furoxan and azide concentrations were measured. Call these F_t and A_t, respectively. At successive equal intervals of time ampoules were removed and the concentrations $F_{t+\Delta}$ and $A_{t+\Delta}$ measured. $(F_{t+\Delta} - F_t)$ represented the furoxan formed in the interval Δ. A_t represented a_0 (measured at time t as the zero of time). $A_t - (F_{t+\Delta} - F_t) = \{(A_t + F_t) - F_{t+\Delta}\}$ represented the concentration of azide at any time $t + \Delta$. This quantity when substituted in the rate expression gave k's in good agreement with k's computed from the azide concentration directly. Further, this method was used at the lower temperatures to find k's in excellent agreement with those calculated from the a_0 obtained by extrapolation. The rate constants are listed in Tables I, II and III.

TABLE I

RATE CONSTANTS FOR PURE LIQUID AZIDE AND DI-*n*-BUTYL PHTHALATE SOLUTION BY GAS-EVOLUTION METHOD

Liquid	Temp., °C.		$k \times 10^5$, sec.$^{-1}$
	64.91		3.705
			3.703
			3.683
		Av.	3.697 ± 0.009
	74.21		10.70
			10.72
			10.67
		Av.	10.70 ± 0.02
Soln., *M*			
0.2143	64.91		2.655
.1186			2.683
.3805			2.633
		Av.	2.657 ± 0.017
0.0628	74.54		7.755
.1255			7.833
.2152			7.945
.0812			7.833
		Av.	7.842 ± 0.05
0.2137	84.39		22.37
.1202			22.42
.0816			22.55
.0814			22.62
.0995			22.45
		Av.	22.48 ± 0.08

Discussion

The rates of decomposition of azide were studied in the pure liquid state and in solution over a concentration range from 2.5×10^{-5} *M* to 0.4 *M*.

TABLE II

RATE CONSTANTS FOR DECOMPOSITION OF AZIDE IN CYCLOHEXANOL

Temp., °C.	Initial concn. of azide $\times 10^5$, *M*		$k \times 10^5$, sec.$^{-1}$ (based on azide dec.)		$k \times 10^5$, sec.$^{-1}$ (based on benzofuroxan formed)
65.18	22.62		2.666		2.604
	22.50		2.661		2.587
	28.01		2.674		2.733
	24.21		2.681		2.741
		Av.	2.671 ± 0.007	Av.	2.666 ± 0.07
70.21	25.19		4.694		4.772
	24.13		4.576		4.726
	25.88		4.691		4.951
	18.92		4.888		4.984
		Av.	4.71 ± 0.08	Av.	4.858 ± 0.11
78.52	23.47		12.02		11.61
	25.22		11.72		12.09
	27.24		12.08		12.14
		Av.	11.94 ± 0.15	Av.	11.95 ± 0.22
87.64	26.98		29.36		30.04
	24.00		30.02		30.56
	26.77		29.90		30.02
		Av.	29.76 ± 0.27	Av.	30.20 ± 0.23

TABLE III

RATE CONSTANTS FOR AZIDE DECOMPOSITION IN HEPTANE

Temp., °C.	Initial concn. of azide $\times 10^5$, *M*		$k \times 10^5$, sec.$^{-1}$ (based on azide dec.)		$k \times 10^5$, sec.$^{-1}$ (based on benzofuroxan formed)
65.18	51.22		2.157		2.276
	51.22		2.256		2.176
	49.80		2.234		2.198
	49.80		2.201		2.217
		Av.	2.212 ± 0.03	Av.	2.217 ± 0.03
71.78	49.43		4.648		4.690
	49.43		4.605		4.747
	49.35		4.699		4.585
	49.35		4.697		4.593
		Av.	4.66 ± 0.04	Av.	4.65 ± 0.06
78.52	49.88		9.772		9.916
	49.88		9.872		9.871
	49.64		9.808		9.879
	49.64		9.806		9.909
		Av.	9.814 ± 0.03	Av.	9.894 ± 0.02

The "thermodynamic" quantities for the reaction were calculated from the appropriate equations: the energy of activation and Arrhenius pre-exponential factor from the equation $\log k = \log A - E^\ddagger/2.303RT$; and the enthalpy and entropy of activation from the Eyring equation

$$\log k/T = \log k_B/h + \Delta S^\ddagger/2.303R - \Delta H^\ddagger/2.303RT$$

where k_B is the Boltzmann constant, and h is Planck's constant. They are shown in the tabulation and were calculated from the averages of rate constants obtained in three or four independent experiments, at each of four temperatures; the rate constants are listed in Tables I, II and III.

The energies of activation and the enthalpies of activation are, within the precision of the measurements, the same in all three solvents and even in the molten state. The entropies of activation are,

	Pure liq.	Di-*n*-butyl phthalate soln.	Cyclohexanol soln.	Heptane soln.
$E^{\ddagger}$, kcal./mole	26.6 ± 0.15	26.3 ± 0.2	26.3 ± 0.4	26.6 ± 0.2
$\Delta H^{\ddagger}$, kcal./mole	26.0 ± .15	25.6 ± .2	25.7 ± .4	25.9 ± .2
A (sec.$^{-1}$) × 10^{-12}	6.2 ± .4	2.7 ± .3	2.4 ± .5	3.4 ± .3
$\Delta S^{\ddagger}$, e.u.	−2.2 ± .4	−3.8 ± .6	−3.7 ± .7	−3.5 ± .5

similarly, invariant to the nature of the solvent, and negative. The difference between the entropy of activation in the liquid decomposition and that in solution is greater than experimental error and probably represents a real difference in solvent–solute interaction.

In an attempt to determine to what extent the solute–solvent interaction is responsible for the negative sign of the entropy of activation, a study of the decomposition in the mixed solvent system, cyclohexanol–heptane was made (see Table IV). A plot of the log of the rate constant *versus* the log of the volume fraction of the more polar constituent of the solvent pair, cyclohexanol–heptane, gave a straight line with a slope of less than 0.1. Hudson and Saville,[7] in a study of solvent participation in kinetics, developed an equation which related the number of solvent molecules participating in the activated complex to the composition of the binary solvent by the equation

$$\log k = n \log v + c$$

k is the rate constant and v is the volume fraction of the more polar component of the binary solvent; n is the number of molecules of the more polar component involved in the transition state. The value of $n = 0.1$ obtained in this study suggests little or no solvation of the azide. The *o*-nitrophenyl azide has already, by virtue of its structure, a built-in solvation,[8] decreasing the need for participation of solvent molecules in the transition complex.

TABLE IV

RATE CONSTANTS FOR AZIDE DECOMPOSITION IN HEPTANE–CYCLOHEXANOL

Mole fraction cyclohexanol	Vol. fraction cyclohexanol (measured at 25°)	Dielectric constant, D (measured at 25°)	$k \times 10^5$, sec.$^{-1}$ (based on azide) 74.74°	78.52°
0	0	1.90	6.60	9.81
0.234	0.180	2.46	6.87	10.55
.439	.360	4.12	7.40	10.84
.676	.600	8.26	7.79	11.54
1.000	1.000	16.10	7.82	11.94

Nevertheless, the changes with solvent composition, though small, in the reaction rate constant, as indicated in Table IV, suggest that there is some solvent effect. A plot of log k *versus* $(1 - D)/(1 + D)$ for the solvent system, cyclohexanol–heptane, gave a straight line, within the limits of measurement of the k's. The term $(1 - D)/(1 + D)$ is the term proposed by Laidler and Eyring[9] for dipole–dipole interaction. A plot of log k *versus* $1/D$ is somewhat less satisfactory, since the $1/D$ term arises when higher order terms in the expansion of the $(1 - D)/(1 + D)$ are neglected, *i.e.*, when D is large. In these experiments D varied from 1.90 (heptane) to 16.1 (cyclohexanol). It seems clear that the solvent effect may change the magnitude, but hardly the sign, of the entropy of activation for this reaction. The negative value is indicative of the formation of a cyclic transition state in the decomposition of *o*-nitrophenyl azide to benzofuroxan and nitrogen.

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[7] R. F. Hudson and B. Saville, *J. Chem. Soc.*, 4114 (1955).

[8] J. F. Bunnett and R. J. Morath, THIS JOURNAL, **77**, 5051 (1955).

[9] (a) S. Glasstone, K. J. Laidler and H. Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., Inc., New York, N. Y., 1941; (b) K. J. Laidler and P. A. Landskroener, *Trans. Faraday Soc.*, **52**, 200 (1956).