appropriate wave length in the 340–380 mμ region were followed to the time of equilibration. The concentrations of free chlorine and of iodobenzene dichloride throughout the runs were calculated from measured optical densities using the extinction coefficients given in Tables I and II.

The equilibrium constants, $K = k_1/k_2$, for each run were calculated from equilibrium readings. The individual rate constants for the forward and reverse reaction are also related by differential equation 9.

$$-\mathrm{d}(C_6H_5ICl_2)/\mathrm{d}t = k_1(C_6H_5ICl_2) - k_2(C_6H_5I)(Cl_2) \quad (9)$$

A useful integrated form of equation 9 is given in equation 10, in which $a = (C_6H_5ICl_2)_i$, $b = -2(C_6H_5ICl_2)_i - K$ and $A = (C_6H_5ICl_2)$. The

$$\ln \frac{2A + b - \sqrt{b^2 - 4a}}{2A + b + \sqrt{b^2 - 4a}} - \ln \frac{2a + b - \sqrt{b^2 - 4a}}{2a + b + \sqrt{b^2 - 4a}} = k_2 t \sqrt{b^2 - 4a} \quad (10)$$

constants k_2 were determined from the slopes of the linear plots of the left-hand term of equation 10 *vs.* time. The results of these runs are summarized in Table VI, in which the values of k_1 and K for the several runs at 25.2 and 45.6° are listed along with equilibrium values of the optical densities of the reaction mixtures.

TABLE VI

RATE CONSTANTS AND EQUILIBRIUM CONSTANTS FOR THE DECOMPOSITION OF IODOBENZENE DICHLORIDE

$10^3 \times$ $(C_6H_5ICl_2)$, moles/l.	λ,[a] mμ	d_{eq}	$10^3 k_1$, sec.$^{-1}$	$10^3 K$,[b] moles/l.	t, °C.
13.7	380	0.900	...	1.47	25.2
2.73	340	.340	0.139	1.54	25.2
1.37	360	.134	0.148	1.44	25.2
2.75	360	.254	1.24	4.3	45.6
1.37	360	.100	1.30	4.3	45.6

[a] Wave length at which runs were made; 1-cm. absorption cells and an acetic blank were used. [b] Value of $\Delta H^0 =$ 9.9 kcal./mole is calculated from average K values at the two temperatures.

One run also was made at 25.2° in which the change in optical density at 380 mμ of an acetic acid solution originally 2.97×10^{-3} M in iodobenzene and 3.23×10^{-3} M in chlorine was followed to the equilibrium point. An equilibrium constant ($K = 2.0 \times 10^{-3}$ mole/l.), calculated from the equilibrium data for this run, compares favorably with an average value of 1.5×10^{-3} mole/l. for the runs reported in Table VI. Rate constants for this run were evaluated graphically according to equation 10 with, in this case, $a = (C_6H_5I)_i(Cl_2)_i$ and $b = -(C_6H_5I)_i - (Cl_2)_i - K$. The resultant k_1 value, 0.16×10^{-3} sec.$^{-1}$, was also in good agreement with the values listed in Table VI.

Although the values of k_1 reported in Table V are on the average somewhat higher than those in Table VI, the agreement is sufficiently good to support the proposed mechanism for the aromatic chlorinations by iodobenzene dichloride. It is particularly gratifying that the activation energy calculated from rate constants k_1 for the reaction of pentamethylbenzene with iodobenzene at 25.2 and 45.6° (E_a = 20.1 kcal./mole) is almost identical with that calculated from the averages of rate constants for the dissociation of iodobenzene dichloride which are given in Table VI (E_a = 20.2 kcal./mole.)

A few qualitative tests were made to determine the behavior of iodobenzene dichloride in non-polar solvents. Dilute solutions of the dihalide in benzene and in carbon tetrachloride showed no changes in spectra over a several-hour period, an indication that dissociation to form the component materials did not occur. Similarly the ultraviolet spectrum of a benzene solution of the dichloride which contained an excess of cyclohexene remained invariant for several hours, and then the dichloride suddenly disappeared completely from the solution.

The reaction which occurred may well have been radical induced. Certainly, further work on the function of the dihalide as a halogen source in nonpolar media is required to rationalize the results of earlier investigators.[18–20]

Acknowledgment.—The authors are indebted to the National Science Foundation for a grant in support of this research.

(18) G. F. Bloomfield, *J. Chem. Soc.*, 114 (1944).

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[CONTRIBUTION FROM LOYOLA UNIVERSITY OF LOS ANGELES]

Nature of Aliphatic C-Nitroso Compounds. I. Study of the Rate of Dissociation of the Aliphatic C-Nitroso Dimer in Various Solvents

BY JOSEPH R. SCHWARTZ

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The rate of dissociation of two aliphatic nitroso dimers, $(CH_3)_2C(NO)CH_2R$, with R = CH_3 and R = OAc in a series of solvents at several temperatures is reported. From the activation parameters, it is concluded that the inductive effect is mainly responsible for rate trends and solvent effects observed.

Introduction

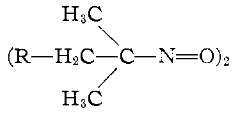
It has been known for some time that many aliphatic C-nitroso compounds exist in the solid state as dimers and, when dissolved in various solvents, dissociate into blue monomers at a measurably slow rate.[1,2] Crystal studies on the dimer show that the N–N distance is between the single- and

(1) Bamberger and Seligmann, *Ber.*, **36**, 692 (1903).

(2) N. V. Sidgwick, "Organic Chemistry of Nitrogen Compounds," Oxford University Press, London, 1942, p. 204.

double-bonded values.[3] Recent spectral evidence on some substituted aromatic C-nitroso compounds has yielded information on the effect of substitution on the monomer–dimer equilibrium in the dissolved state and in the solid state. The ground and excited electronic states for both the monomer and dimer were identified from absorption spectra.[4]

It is of interest to determine more specifically the nature of the bonding forces in the dimer and to gain further insight into the rate of monomer formation. Reported herein is a preliminary investigation of these questions. The rate of monomer formation of the tertiary aliphatic nitroso compounds in a series of solvents of varying dielectric constant and hydrogen bonding ability and at various temperatures has been measured.


$$(R{-}H_2C{-}C(CH_3)_2{-}N{=}O)_2$$

I, R = CH_3COO–

II, R = H_3C–

Experimental

Preparations. I. 2-Methyl-2-nitroso-1-acetoxy-propane.—One hundred and seven grams of 2-methyl-2-nitro-1-propanol (Matheson, Coleman and Bell P1242), m.p. 93–95°, was added to 98 g. of acetic anhydride and the mixture was refluxed for 0.5 hr. One hundred and forty-eight grams of the acetate (81% yield, b.p. 125–127° (30 mm.)) was reduced with 130 g. of zinc dust added portionwise to the acetate in 500 ml. of water containing 200 g. of ammonium chloride. The reduction mixture was cooled, filtered free of solids and 93 g. of potassium dichromate in 200 ml. of 2 *N* sulfuric acid was added, whereupon oxidation of the hydroxylamine to the nitroso compound occurred,[5] as indicated by the presence of the blue color of the I monomer. The solution was extracted with two 250-ml. portions of ether. The ether layer was washed several times with water and dried over anhyd. sodium sulfate. The ether was removed with aspirator vacuum at room temperature. The nitroso acetate I was recrystallized twice from 60–90° boiling range petroleum ether: m.p. 67–69°. *Anal.* Calcd. for $C_6H_{11}NO_3$: C, 49.63; H, 7.64. Found: C, 49.32; H, 7.48. The absorption maximum at 674 mμ, $\epsilon(C_6H_6)$ = 13.9, of the monomer was used to follow the rate of dissociation, since the dimer does not absorb at this wave length.

II. 2-Ethyl-2-nitrosopropane.—*t*-Amylurea (Matheson, Coleman and Bell P5547) was hydrolyzed in diethylene glycol with sodium hydroxide,[6] and the *t*-amylamine so obtained was oxidized to the nitro compound following the directions of Kornblum and Clutter.[7] The nitro compound was reduced to the hydroxylamine and oxidized to the nitroso compound II, using the procedure described under the preparation of I above. Due to the great volatility of the nitroso compound, the ether solution extract of I was evaporated slowly at room temperature under a 20-plate column. A blue-white residue remained. This (approx. 1 g.) was taken up in 8 ml. of isopentane and cooled to −80°, whereupon a white solid precipitated out in a few seconds. This was filtered off and air-dried. Recrystallization from the same solvent yielded a material of m.p. 50.3–51.2°; Bamberger and Seligmann[1] report 50.0–50.5°. In no case was better than 10% yield obtained. Note: several attempts to prepare these aliphatic nitroso compounds in any recoverable yield by method of Bamberger and Seligmann[1] were unsuccessful for 2-methyl-2-nitrosopropane and 2-methyl-2-acetonyl-nitrosopropane (oxidation of the corresponding amine with Caro acid). The absorption maximum at 680 mμ, $\epsilon(C_6H_6)$ 20.4, of the monomer was used to follow the rate of dissociation since here, also, the dimer does not absorb at this wave length.

Measurement of the Dissociation Rate.—A Beckman DU model spectrophotometer was fitted with a special water-tight, pitch-lined compartment, having soft glass windows, so as to function as part of the instrument, and constant temperature water was circulated through this compartment. The temperature was maintained constant to within a variation of 0.01°. Samples of solvent of approximately 3 ml. each were placed in 3 test-tubes, tightly stoppered and allowed to thermally equilibrate. Approximately a 10-mg. sample of the finely powdered nitroso compound was added to the first test-tube, the tube then being stoppered, covered with a cloth to insulate thermally and shaken violently to dissolve the nitroso compound rapidly and transferred to a 1.00-cm. path length Corex cell already in the compartment and at thermal equilibrium. The cell was stoppered. The $t = 0$ for the dissociation was taken as 1 second after the solid was added to the tube, it having previously been determined that approximately this time was necessary for solution of the substance. In exactly the same manner, the other two cells were filled at exactly 1-minute intervals, with successively increasing sample sizes to furnish multiplicate determinations.

The reaction showed good first-order behavior, within experimental error. The reaction was followed for 2 half-lives or more, except where indicated in parentheses in the figures for the rate constants in Tables I and II. Attempts to follow the reaction in acetic acid were unsuccessful, because no clear first-order plot was obtained: the earlier part of the run was first-order, followed by a break in slope and a curving off from linearity. Redetermination of several of the rate constants on other occasions under the same conditions gave the reproducibility indicated in the table; k and the activation parameters were calculated from the data: k by the least squares method, ΔH^* by the Arrhenius plot of log k *vs.* $1/T$, and ΔS^* from the Eyring absolute rate equation, using k at a given T and ΔH^*.

TABLE I

RATE OF DISSOCIATION OF 2-METHYL-2-NITROSO-1-ACETOXY-PROPANE DIMER

Solvent		k_1, sec.$^{-1}$	
	12.88	18.00	25.00
$C_6H_5NO_2$ (36.1)[a]		0.048	0.149
MeOH (33.1)		.0425	.099
$AcCH_3$ (21.4)		.054	.145
$AcOC_2H_5$ (5.0)		.069	.188
$CHCl_3$ (5.0)	0.0153	.032	.087
C_6H_6 (3.1)		.081	.234

[a] Dielectric constant of solvent at 20; source "Internatl. Critical Tables."

TABLE II

RATE OF DISSOCIATION OF 2-ETHYL-2-NITROSOPROPANE DIMER

In acetone +5% water, k_1 = 0.0046 min.$^{-1}$ at 12.88.

Solvent		k_1, sec.$^{-1}$	
	12.88	18.00	25.00
$C_6H_5NO_2$ (36.1)[a]		0.0195	0.0463
MeOH (33.1)	0.0048(50%)[b]	.0088	.025
$AcCH_3$ (21.4)	.0094		.053
$AcOC_2H_5$ (5.0)	.0112	.0233	.0609
$CHCl_3$ (5.0)	.0048[c]	.0059	.0156
C_6H_6 (3.1)	.0122	.026	.072

[a] Dielectric constant of solvent at 20°; source "Internatl. Critical Tables." [b] Extent of reaction followed: where not indicated, this is 75% or more. [c] This reaction was run at 12.80°.

These nitroso compounds in ether solution gradually decolorized upon standing in direct sunlight, in agreement with the observation of Bamberger and Seligmann.[1] Their further observation that freshly dissolved dimer dissociates more slowly if first exposed to light is under study at the present time. Because of these facts, the nitroso solid compounds were stored in the refrigerator, and the solutions were not exposed to strong light at the beginning of the

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[3] C. Darwin and D. Hodgkin, *Nature*, **166**, 827 (1950).

[4] K. Nakamoto and R. E. Rundle, THIS JOURNAL, **78**, 1113 (1956).

[5] P. Tarte, *Bull. soc. chim. Belge.*, **63**, 525 (1954).

[6] *Org. Syntheses*, **29**, 21 (1949).

[7] N. Kornblum and R. J. Clutter, THIS JOURNAL, **76**, 4494 (1954).

runs. The solutions at final equilibrium (dissociation equilibrium) obeyed Beer's law if the solutions were kept more dilute than optical density corresponding to 1.5 units. In all cases under study the optical density was less than 1.5 units for the infinity value.

Results

In Tables I and II are reproduced the results of this investigation at 12.88°, 18.00° and 25.00°, respectively, in the solvents nitrobenzene, acetone, methanol, ethyl acetate, chloroform and benzene. The solvents used in this investigation were reagent grade quality and were used as obtained from J. T. Baker Chemical Co.

TABLE III

ACTIVATION PARAMETERS FOR DISSOCIATION OF I AND II

Solvent	H, kcal./mole	S, e.u.	Solvent	H, kcal./mole	S, e.u.
Compound I			Compound II		
$C_6H_5NO_2$	28.1	32.1	$C_6H_5NO_2$	13.4	10.0
MeOH	20.9	7.6	MeOH	23.2	13.3
$AcCH_3$	21.4	9.4	$AcCH_3$	27.5	28.8
$AcOC_2H_5$	28.2	33.1	$AcOC_2H_5$	25.2	21.3
$CHCl_3$	24.2	18.0	$CHCl_3$	18.6	15.5
C_6H_6	23.5	17.2	C_6H_6	24.9	20.6

Discussion

It may be noted that there is definitely smaller entropy of activation for I in the polar solvents methanol and acetone, indicating that solvent is effectively associated with the bond about to break in the dissociation. Nitrobenzene seems to be particularly effective in assisting the bond to break in the case of II. It may be noted that the solvents have been ordered according to decreasing dielectric constant. No trend seems evident here. Figure 1 shows that for I, ΔH^* is a good linear function of ΔS^*, but this relationship shows a good deal of scatter for II. Figure 2 shows the plot of k_1 for I *vs.* k_1 for II at 25° in various solvents and indicates a fairly linear relationship, with slope = 0.270 ± 0.116 (95% confidence interval), for the straight line through the origin. The line was made to pass through the origin, since, if the Eyring equation is assumed to hold

$$k_1 = \frac{kT}{h} \exp(-\Delta F^*/RT), \text{ then}$$

$$k_1(\text{I})/k_1(\text{II}) = \exp(-\Delta\Delta F^*/RT)$$

which means that the k_1's are linear functions of one another at a given temperature and that the intercept is 0. On the basis of this line, r, the coefficient of correlation = 0.575, and $\Delta\Delta F^*$ was calculated from the mean slope to be 0.78 kcal./mole. Thus, in all the solvents studied, ΔF^* for I is greater by this amount than ΔF^* for II. This is taken to mean that less organized-energy is needed in the dimer to break the N–N bond in dissociating partially to the transition state and that this must be mainly related to the inductive pull of electrons in the acetoxy group, and perhaps it may be stated that this inductive pull contributes a definite amount of energy to the organized states (organized along the direction in which the bond breaks).

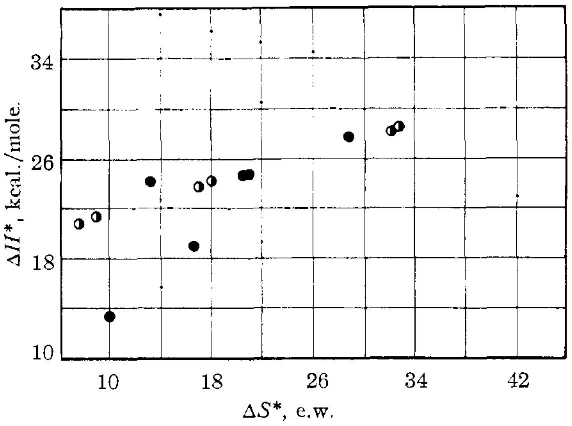

Fig. 1.—Correlation of ΔH^* and ΔS^*: ◐, I; ●, II.

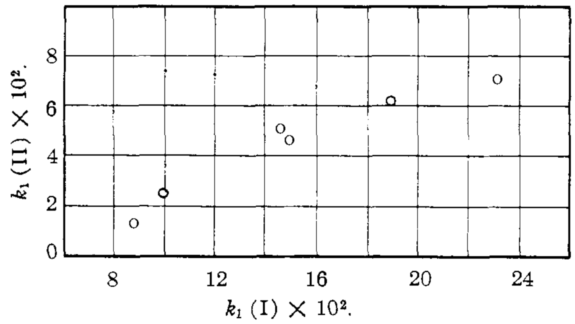

Fig. 2.—Correlation of k_1 of I with k_1 of II in various solvents, at 25.00°.

If there were any steric effects involving solvents, then some of the solvents might be expected to deviate from this line markedly. Since no strong deviation is observed, it suggests that no steric effects seem to enter the picture. Preliminary work is in progress to determine the extent of this factor using R = *t*-butyl.

Nakamoto and Rundle[4] suggest that electron-donating groups stabilize the monomer of aromatic nitroso compounds through a resonance mechanism. In the two compounds studied here, only inductive effects are possible between the substituent and the reaction center and, since no equilibrium constants were determined, it can only be concluded that electronegative groups would make the unshared pair of electrons on the nitrogen atom less available for dimer formation, and hence there might be a contribution from this source to lower the activation energy for monomer formation. The fact that N–N–O compounds do not dimerize, however, is in keeping with these ideas, since nitrogen is quite strongly electronegative and probably would keep the unshared pair on the nitroso-nitrogen unavailable for dimer-bonding.

In a preliminary experiment the rate of dissociation of the pseudonitrole, $(CH_3)_2(NO)(NO_2)$, and nitrosobenzene in benzene were found to be too rapid to measure. This probably indicates that the N–N dimer bond is quite weak. It is a well known fact that negative substituents decrease the stability of these dimers. For example, $(CH_3)_2$-$CCl(NO)$[5] and $(CF_3)_2C(F)(NO)$[8] are both known only as the blue monomer.

Acknowledgment.—The author is much indebted to Research Corporation for the grant-in-aid which made this research possible.

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(8) J. Banus, *Nature*, **171**, 173 (1952).