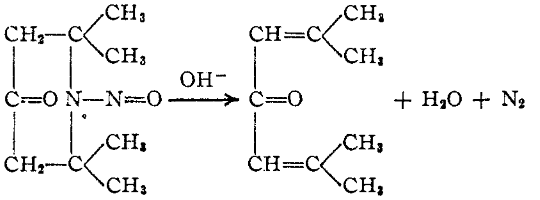
[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF NEW YORK UNIVERSITY]

Temperature and Dielectric Constant Effects in the Decomposition of Nitrosotriacetoneamine

BY CECIL V. KING AND FABIAN LIONETTI

The hydroxyl ion catalyzed decomposition of nitrosotriacetoneamine has been studied by a number of investigators and has been used in this Laboratory as a means of measuring hydroxyl ion concentrations.[1] The reaction may be formulated as



(1)

The salt effect has been shown to be normal for this type of reaction. Since the kinetics are well known it was decided to measure the rates over a range of temperature and dielectric constant for comparison with the various pertinent theories.

Experimental

The rate was determined by measuring the pressure of the nitrogen evolved as before.[1] Five temperatures were used: 14.9, 19.9, 24.9, 29.9 and 34.9°, each ±0.02°. The temperature coefficient is approximately 1.1% per 0.1° throughout, and all rate constants were arbitrarily increased by this amount to correspond to round temperatures. Dioxane–water mixtures up to 40% dioxane (by volume) were used, the dioxane being purified as described by Beste and Hammett.[2] All solutions were made with carbonate-free sodium hydroxide and carbon dioxide-free water.

The same concentration of sodium hydroxide, 0.04 *M*, was used in all experiments. In addition to experiments with no other added electrolyte another complete series was run with 0.16 *M* sodium chloride present. Enough rates were run with intermediate salt concentrations to show that the salt effect is linear with ionic strength at all dioxane concentrations.

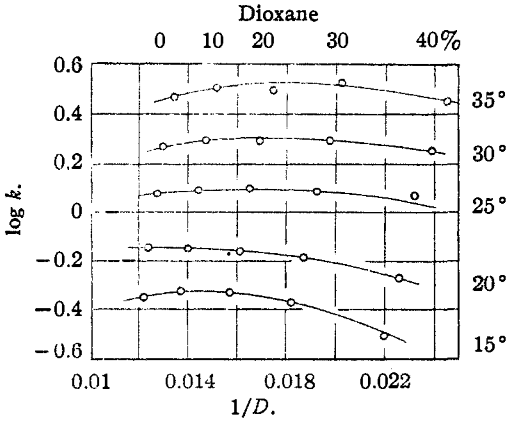


Fig. 1.—Logarithm of rate constant *vs.* reciprocal of dielectric constant.

All experiments were run at least in duplicate and only averages are reported. Attempts were made to measure the rates in 50 and 60% dioxane; the results were erratic, and it was noticed that at the lower temperatures droplets of a second phase separated. Some of the rates obtained at higher temperatures could be plotted on a continuation of the curves of Fig. 1.

Results

Logarithms of the rate constants obtained are given in Table I. These are second order constants, *i. e.*, the first order constants measured experimentally have been divided by 0.04, the sodium hydroxide concentration. The values in water are considerably lower than those found by Francis and Geake,[3] especially at 15 and 20°, but agree within 1 or 2% with values found by Kilpatrick[4] under similar conditions at 15, 20 and 30°. Kilpatrick found the primary salt effect to be affected very little by the temperature or the medium, and the values in Table I, though not highly consistent, verify this conclusion.

TABLE I

RATE CONSTANTS IN NITROSOTRIACETONEAMINE DECOMPOSITION

T, °C.	Dioxane, vol. %	log *k* $\mu = 0.04$	log *k* $\mu = 0.20$
15	0	$\bar{1}.656$	$\bar{1}.642$
	10	.675	.634
	20	.672	.566
	30	.628	.542
	40	.498	.386
20	0	$\bar{1}.854$	$\bar{1}.810$
	10	.854	.805
	20	.839	.805
	30	.816	.708
	40	.732	.684
25	0	0.079	0.053
	10	.093	.053
	20	.100	.068
	30	.090	.076
	40	.072	.025
30	0	0.270	0.250
	10	.295	.248
	20	.295	.253
	30	.288	.243
	40	.255	.233
35	0	0.462	0.412
	10	.502	.444
	20	.496	.436
	30	.522	.474
	40	.447	.420

The logarithms of the constants at 0.04 μ are plotted *vs.* the reciprocal of the dielectric constant

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[1] King and Marion, THIS JOURNAL, **66**, 977 (1944).

[2] Beste and Hammett, *ibid.*, **62**, 248 (1940).

[3] Francis and Geake, *J. Chem. Soc.*, **103**, 1772 (1913).

[4] Kilpatrick, THIS JOURNAL, **48**, 2091 (1926).

in Fig. 1. To establish a point of reference in which rates are freed from the ionic strength part of the electrostatic effects it is customary to extrapolate constants, especially in ion–ion reactions, to zero ionic strength. In this ion–neutral molecule reaction the extrapolated values would differ very little from those used.

Energy and Entropy of Activation.—Values of log k were read from the curves of Fig. 1, plotted *vs.* $1/T$ and straight lines drawn through the points to obtain the experimental activation energies, $E_{\text{exp.}}$. This was done for iso-composition media (Table II) and for iso-dielectric media (Table III). The Arrhenius constant A was calculated from the equation

$$\log A = E_{\text{exp.}}/2.3RT + \log k \qquad (2)$$

The activation entropy ΔS^* was calculated from the Eyring equation[5]

$$\Delta S^* = 2.3\,R \log A - 2.3\,R \log eRT/Nh \qquad (3)$$

where $\log eRT/Nh = 15.01$ at 25° using the minute as time unit. The free energy ΔF^* was obtained from the relation

$$\Delta F^* = 2.3\,RT \log eRT/Nh - RT - 2.3\,RT \log k \qquad (4)$$

These values are given for 25° only, since the relations at the other temperatures would be similar. The experimental values are not accurate enough to detect any change in energy of activation with temperature, though values of ΔS^* other than zero indicate that there should be such a change. The small change of ΔF^* with dielectric constant reflects the comparatively small change in rate constants.

TABLE II

ACTIVATION ENERGIES AT 25° IN ISO-COMPOSITION MEDIA

Dioxane, vol. %	log k, 25°	$E_{\text{exp.}}$	log A	ΔS^*	ΔF^*
0	0.079	16640	12.29	−12.4	19760
10	.094	16960	12.54	−11.4	19730
20	.100	17470	12.92	− 9.6	19720
30	.090	18290	13.51	− 6.9	19740
40	.040	20070	14.78	− 1.1	19790

TABLE III

ACTIVATION ENERGIES AT 25° IN ISO-DIELECTRIC MEDIA

D	log k, 25°	$E_{\text{exp.}}$	log A	ΔS^*	ΔF^*
80	0.076	15770	11.66	−15.3	19740
70	.093	16550	12.24	−12.7	19730
60	.098	17420	12.89	− 8.7	19710
50	.085	18970	14.01	− 4.6	19740

Discussion

The Dielectric Constant Effect.—It is at once obvious that no present theory can account quantitatively for the effect of changing dielectric constant on the rate. The problem is to calculate the change in the activity coefficient term in the general rate expression

$$\log k = \log k_0 + \log \alpha_A \alpha_B/\alpha^* \qquad (5)$$

where the α's are the activity coefficients of the reactants and the critical complex. We may choose an arbitrary reference point for k_0, such as the aqueous solution at each temperature or a hypothetical aqueous solution with a dielectric constant of 80 at each temperature. If the critical complex could be considered a normal ion with the same activity coefficient as the parent (hydroxyl) ion in all media the rate would depend on the properties of the neutral molecule only. This is unlikely because of the size and structure of the nitrosotriacetoneamine molecule (equation 1). On the other hand if the activity coefficient of the neutral molecule were independent of the medium the simplified Laidler–Eyring equation[6] should apply

$$\log k = \log k_{D=\infty} + \frac{Z_A^2 \epsilon^2 N}{2DRT}\left(\frac{1}{r_A} - \frac{1}{r^*}\right) \qquad (6)$$

where Z_A is the valence of the hydroxyl ion, r_A and r^* the radii of ion and critical complex respectively. Assuming the ionic radii to be independent of the medium the plot of log k *vs.* $1/D$ should be linear and should have a positive slope if $r^* > r_A$.

Harned and Samaras[7] have attempted to calculate the ratio of activity coefficients in different media. For this type of reaction their calculation leads to the equation

$$\Delta \ln k = K \Delta D \qquad (7)$$

for relatively small changes in dielectric constant, where K should be approximately 0.03. While small additions of dioxane cause an increase in the rate, the increase is far less than calculated from this equation. Harned and Samaras point out that rates in the hydroxyl-ion catalyzed decomposition of diacetone alcohol do not agree with their theory and ascribe this to peculiarities of the hydroxyl ion.

Amis and Jaffé[8] have developed an equation for ion–dipole reactions, which expresses the salt effect as a function of ionic strength and dielectric constant. This equation predicts a negative salt effect for a negative ion–dipole reaction, which is in accord with the salt effect in this reaction, but it predicts a smaller salt effect at lower dielectric constants, which is not evident in our results.

The Activation Entropy.—For the simple collision theory to apply the entropy values as calculated in Tables II and III should have small, constant positive values (since the collision number Z is slightly larger than the frequency factor eRT/Nh). In terms of the collision theory the negative values found would indicate that only a fraction of the collisions with sufficient energy available actually lead to reaction. In terms of the Eyring rate theory they indicate that formation of the critical complex requires considerable rearrangement of the nitrosotriacetoneamine mole-

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(5) Glasstone, Laidler and Eyring, "The Theory of Rate Processes," McGraw-Hill Book Co., New York, N. Y., 1941, p. 417.

(6) Laidler and Eyring, *Ann. N. Y. Acad. Sci.*, **39**, 303 (1940).

(7) Harned and Samaras, THIS JOURNAL, **54**, 9 (1932).

(8) Amis and Jaffé, *J. Chem. Phys.*, **10**, 598 (1942); Amis. Jaffé and Overman, THIS JOURNAL, **66**, 1823 (1944).

cule, with the complex probably having properties similar to those of the reaction products.[9]

It has been shown by LaMer[10] that the activation energy terms, for a reaction involving electrostatic effects, may be divided into three terms. Thus, for the entropy

$$\Delta S^* = \Delta S_0^* + \Delta S_D^* + \Delta S_{\text{In}}^* \qquad (8)$$

where ΔS_0^* is the entropy freed from electrostatic effects, ΔS_D^* is the portion due to the change in dielectric constant from this ideal state, and ΔS_{In}^* the portion due to ionic strength effects. In the present case ΔS_{In}^* may be considered negligible. It has been pointed out by Warner[11] that $\Delta S_D^* = 0$ when temperatures coefficients are measured in iso-dielectric media.

The entropy values of Table III are therefore free of electrostatic effects in the usual sense. The value of ΔS_0^* should, however, be a constant independent of the medium, whether its magnitude meets the requirements of the collision theory or not. Evidently another variable term should be added to equation (8)

$$\Delta S^* = \Delta S_0^* + \Delta S_D^* + \Delta S_{\text{In}}^* + \Delta S_x^* \qquad (9)$$

where ΔS_x^* varies with the medium but is not a normal electrostatic term. In view of the dilute solutions used it cannot correspond to a normal non-electrostatic term such as that in the complete Laidler–Eyring equation (ref. 6, p. 330).

A possible explanation of the variable term ΔS_x^* may be found in the different degrees of hydration of the hydroxyl ion in the different media. Formation of the critical complex must require a simultaneous displacement of the hydration equilibrium. While in a mixed solvent hydrophilic ions tend to remain hydrated, the normal equilibrium must be considerably disturbed. Tables II and III show that the activation energy approaches the expected value in high dioxane concentrations (*i. e.*, $\Delta S^* \rightarrow 0$) and this would correspond to a minimum of hydration displacement in formation of the critical complex. A reaction involving hydrogen ion would be less subject to such an effect because of the greater stability of the hydrated ion in mixed solvents; this is seen in the reaction of hydrogen ion and azodicarbonate ion.[12]

The authors wish to thank Mr. Seymour Zenchelsky and Mr. Myron Lover, who carried out a number of the experiments reported here.

Summary

The rate of decomposition of nitrosotriacetoneamine catalyzed by hydroxyl ion, has been measured at five temperatures from 15 to 35°, in solutions of water and dioxane up to 40% dioxane.

It has been shown that the effect of changing the dielectric constant and temperature does not agree with the simplified forms of present theory. Factors which may cause the deviations have been discussed.

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[9] Ref. (5), pp. 22, 24 and 418.

[10] LaMer, *J. Frank. Inst.*, **225**, 709 (1938).

[11] Warner, *Ann. N. Y. Acad. Sci.*, **39**, 345 (1940).

[12] King and Josephs, This Journal, **66**, 767 (1944).

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Preparation and Polymerization of *p*-Cyanostyrene, *p*-Vinylbenzoic Acid and its Methyl Ester[1,2]

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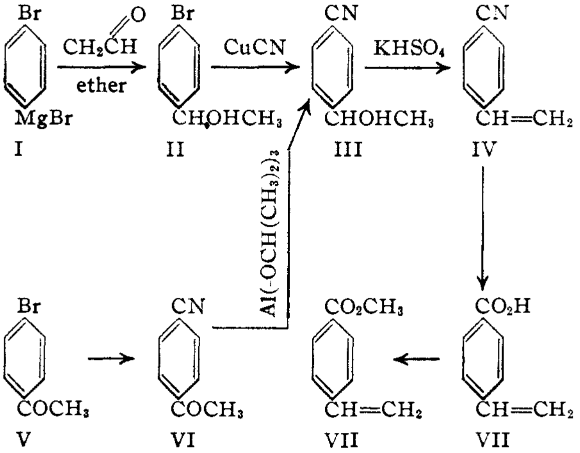
This paper describes the synthesis of *p*-cyanostyrene and its conversion to *p*-vinylbenzoic acid and its methyl ester as outlined in the chart. *p*-Cyanophenylmethylcarbinol (III) was prepared by two routes, one through the Grignard reagent from *p*-dibromobenzene (I) and the other from *p*-bromoacetophenone (V). By either route the final yield was low. The ease with which *p*-cyanostyrene polymerized during its preparation or storage caused considerable difficulty in the synthesis. These new styrene derivatives have been polymerized by standard procedures in order



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[1] A part of the work described in this manuscript was done under Contract RuRSR 95 between Rubber Reserve Company and the University of Illinois.

[2] This is the nineteenth communication on vinyl polymers. For the eighteenth see This Journal, **66**, 475 (1944).