It should be noted that the nitrogen atoms originally contained in the hydrazine remained united in the chain propagation steps and form the end product, nitrogen. Exception is made of the atoms of nitrogen used to form triazane. These will be mixed in the products. If it is desired that this mechanism predict substantially no scrambling of nitrogen atoms in the process, it is only necessary to suppose that relatively few molecules of triazane are used in initiating the chains which are themselves of relatively great length. In any case, the nitrogen atoms of the chloramine molecules which are consumed in the chain propagation steps finally appear in ammonium chloride.

It is reported by Higginson and Sutton[21] as a result of studies using isotopically marked hydrazine that there is no scrambling of nitrogen in the oxidation of hydrazine observed in alkaline solution. The mechanism proposed here conforms to their experimental results if, as has already been suggested, the chains are thought to be long.

They and also Cahn and Powell[22] (following a similar technique) arrive at a mechanism which for the oxidation of hydrazine under these conditions leads from hydrazine by oxidation to the hydrazyl radical, $\cdot$NHNH$_2$. The latter is oxidized further to diazene, NH=NH, which suffers rapid oxidation to nitrogen. This mechanism also predicts no randomization of isotopic nitrogen but has the defect that it does not predict properties usually associated with chain reactions, such as the low temperature coefficient and the induction period found in the present work.

The three mechanisms proposed by Kirke and Browne[23] for the oxidation of hydrazine under most conditions are non-chain processes. They involve among them six hydrogen–nitrogen intermediates, including diazene, tetrazane and two tetrazenes. They do not predict the several extents of randomization of isotopic nitrogen observed by Cahn and Powell[22] using a variety of oxidizing agents at several acidities.

A number of attempts were made to find a sim-

ple relation between the concentrations of reactants and the observed rates of the decomposition reaction. The results were indecisive. Calculations were made to test the free radical chain mechanism proposed in equations 28 through 42. It was not found possible to correlate quantitatively the time for the inflection point in the rate data (Figs. 2 and 3) with the concentrations of the known reactants. A quantitative fit of all the data was not expected since some duplicate experiments gave greatly different induction periods.

However, in view of the large number of phenomena that the mechanism accounts for, it is thought that complications must result from partial heterogeneous character and/or metal catalyzed initiation of the reaction. The mechanism is, in general, consistent with the stoichiometry, the period of induction, the relatively large reaction rate, the temperature insensitivity and the lack of randomization of isotopic nitrogen associated with the decomposition reaction. Further tests of the mechanism of the decomposition reaction are in progress.

Extrapolation to the Water System.—The authors are aware that a considerable measure of extrapolation is necessary in order to extend conclusions based on reactions in liquid ammonia to those in water, and *vice versa*. Such extensions as have been made or inferred are hereby qualified for, as has been pointed out,[24] the reactions in liquid ammonia differ from those in water in several features: (a) the absence of the catalytic effect of trace metal ions to the extent that this effect is observed in water, (b) the absence of an effect of potassium amide on hydrazine yield, (c) the absence of any effect by gelatin and other inhibitors.

(21) W. Higginson and D. Sutton, *J. Chem. Soc.*, 2S7, 1402 (1953).
(22) J. Cahn and R. Powell, This Journal, **76**, 2568 (1954).
(23) R. E. Kirk and A. W. Browne, *ibid.*, **50**, 337 (1928).

(24) R. S. Drago, private communication.

Solvent Effect on a Primary Carbon Isotope Effect—Decarboxylation of Trinitrobenzoate Ion in Water and Ethanol-Water Mixture[1]

By Peter Riesz[2] and Jacob Bigeleisen

Carboxyl carbon, C^{12}-C^{13}, isotope effects have been determined for the decarboxylation of trinitrobenzoate ion in water and 90% ethanol between 30 and 8)°. A small but significant difference is found in the isotope effects in the two solvents. The difference is correlated with solvation effects.

Introduction

The kinetics of decarboxylation of 2,4,6-trinitrobenzoic acid have been studied in ethanol[3] and in

dioxane–water mixtures[4] by Verhoek and Trivich. The rate-determining step was shown to be the unimolecular decomposition of the trinitrobenzoate ion. The rate of decarboxylation was found to increase with decreasing dielectric constant of the

(3) F. H. Verhoek, This Journal, **61**, 186 (1939).
(4) D. Trivich and F. H. Verhoek, *ibid.*, **65**, 1919 (1943).

TABLE I

ISOTOPIC COMPOSITION OF CO_2 SAMPLES FROM THE DECARBOXYLATION OF SODIUM TRINITROBENZOATE SOLUTIONS IN WATER

T, °C.	f	$N_x \times 10^4$ (uncor.)	k_{12}/k_{13}
79.8	0.0563	134.46	1.0328
	.2749	134.82	1.0341
	.4614	135.28	1.0347
	.7756	136.53	1.0345
		Av.	1.0340 ± 0.0006
50.0	0.0651	134.19	1.0353
	.2857	134.54	1.0370
	.4606	134.99	1.0380
	.5580	135.43	1.0369
	.7013	136.19	1.0343
		Av.	1.0363 ± 0.0012
79.8	0.975	138.42	
75.0	.991	138.44	
Tank CO_2		138.37	

TABLE II

ISOTOPIC COMPOSITION OF CO_2 SAMPLES FROM THE DECARBOXYLATION OF SODIUM TRINITROBENZOATE SOLUTIONS IN 90% ETHANOL–10% WATER

T, °C.	f	N_x	k_{12}/k_{13}	f'	N'_x	$(k_{12}/k_{13})'$
30.0	0.0564	135.02	1.0281	0.0425	133.83	1.0380
	.0629	134.99	1.0285	.0492	133.97	1.0368
	.2263	134.93	1.0320	.2149	134.67	1.0341
	.2764	134.84	1.0339	.2658	134.61	1.0359
	.4929	135.19	1.0369	.4854	135.09	1.0378
	.6481	135.78	1.0369	.6429	135.72	1.0375
	.7678	136.50	1.0343	.7644	136.46	1.0347
		Av.	1.0329 ± 0.0029		Av.	1.0364 ± 0.0013
50.0	0.0652	135.26	1.0262	0.0514	134.34	1.0337
	.2775	135.07	1.0317	.2669	134.87	1.0334
	.5027	135.63	1.0322	.4954	135.54	1.0329
	.6452	136.19	1.0310	.6400	136.13	1.0316
	.7578	136.63	1.0312	.7578	136.60	1.0315
		Av.	1.0305 ± 0.0017		Av.	1.0326 ± 0.0008

Ethanol was dried as described by Fieser.[7]

Highly deuterated ethanol-1-d was prepared by mixing ethanol and deuterium oxide (1:1 mole ratio) and distilling off the azeotrope. The same procedure was repeated three times altogether. Finally, the water was removed from the azeotrope.[7] The resulting ethanol-1-d was calculated to be more than 90% deuterated.

Apparatus and Procedure.—The apparatus and procedure were similar to those described by Bigeleisen and Allen[8] except for the method of purifying CO_2. It was not found possible to remove the last traces of volatile impurities in every sample by absorption in base and subsequent regeneration of CO_2. Instead, CO_2 was distilled through spiral traps at $-120°$, and the last traces of impurities were removed by combustion with copper oxide and oxygen at 700° for four hours. In every case the volume of CO_2 before and after combustion was unchanged within experimental error (0.3%). Hence, the dilution of fractionated CO_2 by CO_2 from the combustion of impurities cannot change the 45/44 ratio by more than 0.01%. The absence of any significant effect on the 45/44 ratio due to O^{17} exchange during the combustion was demonstrated by experiments with tank CO_2.

In all experiments using water as the solvent, the concentration of sodium trinitrobenzoate was 0.2 M. For experiments in 90% ethanol–10% water (by volume) the concentration was 0.06 M.

solvent. Thus, the specific rate constant is about one thousand times greater in ethanol than in water at 50°, and the energy of activation is about 9 kcal. lower. The increased distribution of charge in the transition state has been discussed by Glick.[5]

In view of the usefulness of carbon isotope effects in the study of reaction mechanisms in solution, it seems desirable to obtain some information about the effect of solvent. Such data are also of interest in connection with the limits of applicability of the simplified theoretical models,[6] in which solvent interaction is neglected. Because of its remarkable dependence on solvent and its simple kinetics, the trinitrobenzoate decarboxylation is particularly suitable for this purpose. We therefore have studied the carbon isotope effect in water and in 90% ethanol at two temperatures.

Experimental

Materials.—Sodium trinitrobenzoate was prepared by the method of Verhoek.[3] The yield of CO_2 from this material was 99.1% of the theoretical.

Thermostats were controlled to ± 0.02° at 30.00° and 50.00°, to ± 0.10° at 79.8°.

Rates in anhydrous deuterated ethanol-1-d were measured by a method similar to that of Verhoek,[3] using a Beckman pH meter for titrations.

Isotopic Analysis.—Mass spectrometric analyses of CO_2 samples were made on a Consolidated Nier "Isotope Ratio" mass spectrometer. The methods used and the treatment of the experimental data have been described in a previous paper.[9] The total correction of the 45/44 ratio for resolution and O^{17} is 9.82×10^{-4} in these experiments. The results of the analyses and the ratios of the rate constants, k_{12}/k_{13}, calculated from them are given in Tables I and II. The symbols k_{12} and k_{13} refer to reactions in which the carbon of the carboxylate group is C^{12} and C^{13}, respectively. N_x is the observed ratio $C^{13}O_2/C^{12}O_2$ of the cumulative CO_2 sample collected up to a fraction, f, of complete reaction, corrected only for fluctuation of the reference tank CO_2.

For experiments in which 90% ethanol–10% water was used as the solvent, the calculated isotope effect, k_{12}/k_{13}, increases markedly with increasing fraction of decarboxylation. This is shown in Table II. The specific rate constants obtained from the same series of experiments were approximately 20% higher at 5% decarboxylation than at 50%. A trend in k as a function of the amount of reaction is evident. All of these observations are consistent with the assumption

(5) R. E. Glick, *Chemistry and Industry*, 717 (1955).

(6) J. Bigeleisen and M. Wolfsberg, in "Advances in Chemical Physics," Vol. I, I. Prigogine, Editor, Interscience Publishers, Inc., New York, N. Y., 1958, pp. 65–72.

(7) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Company, Boston, Mass., 1941, p. 358.

(8) J. Bigeleisen and T. L. Allen, *J. Chem. Phys.*, **19**, 760 (1951).

(9) A. A. Bothner-By and J. Bigeleisen, *ibid.*, **19**, 755 (1951); see also ref. 6, pp. 35–52.

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Table III

Specific Rate Constants[a] in 90% Ethanol at 30°
Correction for 1.45% Impurity in TNB

f	$k \times 10^5$, sec.$^{-1}$	f'	$k' \times 10^5$, sec.$^{-1}$
0.0564	1.93	0.0425	1.43
.0629	2.07	.0492	1.61
.2263	1.69	.2149	1.59
.2764	1.48	.2658	1.34
.4929	1.60	.4854	1.56
.6481	1.65	.6429	1.63

Av. 1.53 ± 0.09

[a] k = observed rate constants; k' = corrected rate constants.

that the sodium trinitrobenzoate used in these experiments contains a small amount of another substance which decarboxylates rapidly compared to trinitrobenzoate. The CO_2 from this source will be essentially unfractionated and will have a tenfold greater dilution effect in a sample at 5% decarboxylation than one at 50%. Hence the effect on the observed isotopic ratio will be most pronounced for samples of low conversion.

All data in Table II were recalculated assuming that the trinitrobenzoate contains 1.45% of such an impurity and that the rate of production of CO_2 from this source is rapid compared to the main reaction. The corrected isotope effect, $(k_{12}/k_{13})'$, does not show large non-random drifts as a function of the amount of decarboxylation. The same correction also results in improved agreement between specific rate constants calculated from samples at 5 and 50% decarboxylation (Table III).

Results and Discussion

The C^{12}-C^{13} decarboxylation isotope effects in trinitrobenzoate are compared with those for the decarboxylation of other monobasic acids in Fig. 1. The results obtained for aqueous solutions are quite close to those found for the decarboxylation of mesitoic acid in sulfuric acid and trichloroacetate ion in water. The isotope effect found for trinitrobenzoate ion in 90% ethanol–10% water is significantly lower.

An experiment was designed and carried out to investigate the possible role of the hydroxylic hydrogen in ethanol in determining the rate. The rate of decarboxylation of trinitrobenzoate ion in anhydrous deuterated ethanol was found to be within 3% that in anhydrous ordinary ethanol at 35°. The change in the carbon isotope effect in going from water to ethanol should therefore be correlated directly with the differences in enthalpy and entropy of activation in the two media.

The large positive entropy of activation for aqueous solutions and the fact that the entropy of activation is smaller in alcohol (cf. Table IV) is indicative of the fact that the ground state is the more highly solvated. In water solution charged reso-
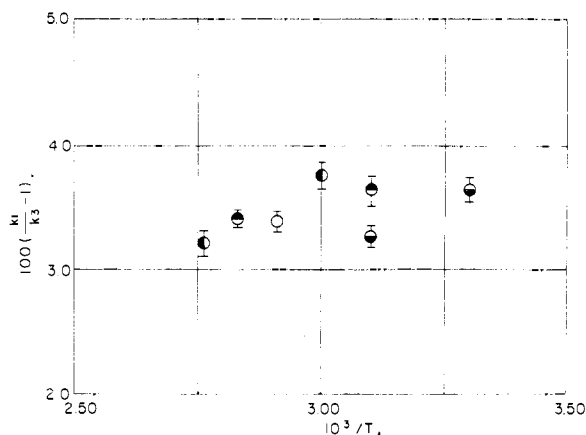
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Fig. 1. — C^{12}-C^{13} isotope effects in the decarboxylation of mono-basic acids as a function of temperature: ◑, mesitoic acid; ○, trichloroacetate ion; ◑, trinitrobenzoate ion in water; ◑, trinitrobenzoate ion in 90% ethanol–10% water.

nance forms are stabilized by solvation. Such resonance forms will serve to give the bond between the aromatic ring and the carboxylate group some double bond character. The solvation in the

Table IV

Decarboxylation of Trinitrobenzoate

Solvent	$k_{30°} \times 10^7$, sec.$^{-1}$	$\Delta H^{\ddagger}$, kcal.	$\Delta S^{\ddagger}$, e.u.
H_2O	5.6	35.8 ± 0.4	25
90% EtOH	2950	27.4 ± 1.0	
100% EtOH	5540	27.4 ± 1.2	12

transition state will also be different in the two media. An estimate of the magnitude of the solvation effect can be made by the relation[10]

$$\frac{k_1}{k_3} = \left(\frac{\nu'^{\ddagger}}{\nu^{\ddagger}}\right)\left[1 + \frac{\bar{\gamma}}{24}\left(\frac{\hbar c}{kT}\right)^2 \sum_{i=1}^{3}(\mu_{C^{12}} - \mu_{C^{13}})(a_{ii} - a_{ii}^{\ddagger})\right]$$

where $\mu_{C^{12}}$ and $\mu_{C^{13}}$ are the reciprocals of the masses of C^{12} and C^{13}, respectively. It has been shown[11] that this equation gives a reasonable fit to the data on the decarboxylation of monobasic acids. The major contribution to k_{12}/k_{13} comes from the zero point energy effect. A decrease of 10% in $(a_{ii} - a_{ii}^{\ddagger})$ in going from water to ethanol suffices to explain the observed change in isotope effect. Such a change does not seem unreasonable in a system with such large solvation.

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(10) Ref. 6, equation (II.30).
(11) Ref. 6, Fig. 7.

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