[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE SPRAGUE ELECTRIC CO., NORTH ADAMS, MASS.]

Ionic Association in the Ethanolysis of N-Benzyl-N,N-dimethyl-*p*-toluidinium Bromide

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The ethanolysis of N-benzyl-N,N-dimethyl-*p*-toluidinium bromide has been studied. Rates have been measured for the over-all conversion of this salt to benzyl ethyl ether plus N,N-dimethyl-*p*-toluidinium bromide as well as for other pertinent reactions. The mechanism employed to describe the observed kinetics involves benzyl bromide as an intermediate and relies heavily on the concept of ionic association. The ion-pair concept is also invoked in a discussion of some other related reactions.

In a previous report from this Laboratory,[1] it was shown that the alcoholysis of benzyldimethylanilinium ion involves the anion associated with it, as demonstrated by the grossly different rates of solvolysis observed with the bromide, nitrate and picrate. It was suggested that the mechanism for the solvolysis of the bromide might involve SN2 attack by bromide ion on benzyldimethylanilinium ion to form benzyl bromide and N,N-dimethylaniline with subsequent alcoholysis of the benzyl bromide.

The rate data previously presented for this reaction were not considered sufficiently precise for testing this mechanism. Experimental inaccuracies in this work resulted from the early development in the reaction mixture of a persistent purple color which obscured the end-point in the titration of the acid formed by the solvolysis reaction. This difficulty has been obviated by selecting for study another salt, N-benzyl-N,N-dimethyl-*p*-toluidinium bromide, and the present paper is concerned with the rates, products and mechanism of solvolysis of this salt in absolute ethanol at 50.8 ± 0.1° and at 71.7 ± 0.1°.

Experimental

Materials.—Absolute ethanol, obtained from the U. S. Industrial Chemicals Co., was distilled from calcium hydride before use.

Eastman Kodak Co. white label N,N-dimethyl-*p*-toluidine was refluxed 3 hours with acetic anhydride and distilled under nitrogen. A middle cut, b.p. 92° (12 mm.), was redistilled under nitrogen and a middle fraction, b.p. 98° (17 mm.), was collected. Redistillation of this fraction under nitrogen afforded a middle cut of b.p. 93–94° (11 mm.) which was stored under nitrogen with some zinc turnings.

Eastman Kodak Co. white label benzyl bromide was distilled under nitrogen, a middle cut, b.p. 80–82° (12 mm.), being redistilled with a middle fraction, b.p. 85° (16 mm.), being retained and stored under nitrogen.

Benzyldimethyl-*p*-toluidinium bromide was prepared by treating an equimolar mixture of benzyl bromide and N,N-dimethyl-*p*-toluidine in acetone at room temperature for 20 hours. The product was precipitated by addition of ether and was crystallized three times from ethanol; yield 90%, m.p. 158–160° dec.

Anal. Calcd. for $C_{16}H_{20}NBr$: Br, 26.10. Found: Br, 26.11.

Rate Measurements.—Procedures for the determination of the rates of ethanolysis of the quaternary ammonium bromide and of benzyl bromide have been described previously.[1] In the present work, the acid produced was determined either by a *p*H titration or by titrating to a phenolphthalein end-point.

To measure the rate of reaction of benzyl bromide with N,N-dimethyl-*p*-toluidine, aliquots (5 ml.) of a determinate solution of benzyl bromide in ethanol were pipetted into ampoules which were cooled in an ice-bath. Aliquots (5 ml.) of a determinate solution of N,N-dimethyl-*p*-toluidine in ethanol were then pipetted into the same ampoules. The ampoules were sealed, shaken and inserted into a constant temperature bath, where vigorous shaking was continued for an additional 2 minutes. Temperature was maintained constant within ±0.1°. The ampoules were withdrawn at appropriate time intervals and cooled in ice-water. The contents were poured into 50 ml. of benzene in a separatory funnel, and the benzene solution was extracted with 30 ml. of 1:4 nitric acid and twice more with water. The combined aqueous extracts were analyzed for bromide ion by the Volhard method.

Isolation of Products.—A solution of benzyldimethyl-*p*-toluidinium bromide (9.19 g., 0.03 mole) in anhydrous ethanol (200 ml.) was refluxed for 185 hours. Concentrated HCl (10 ml.) was added, and ethanol (125 ml.) was distilled from the reaction mixture at atmospheric pressure. The residue was poured into water (500 ml.) and extracted three times with benzene and once with hexane. The combined organic extracts were dried over $MgSO_4$, and the solvents were removed through a Vigreux column. Distillation of the residue gave 2.39 g. (72%) of a clear liquid, b.p. 70–75° (17 mm.), which was shown to be benzyl ethyl ether by the coincidence of its infrared spectrum with that of an authentic sample. The acidic layer was made strongly basic and was extracted three times with ether and once with hexane. The combined organic layers were dried over $MgSO_4$, and the solvents were distilled through a Vigreux column. Excess picric acid in ethanol added to the residue gave 9.56 g. (88%) of yellow crystals, m.p. 127–128°. Crystallization from methanol raised the m.p. to 128–129°; mixed m.p. with authentic picrate of N,N-dimethyl-*p*-toluidine, 128–129°.

Detection of Ethyl Bromide and Ethyl Ether.—In both of these experiments the apparatus used was a Perkin-Elmer model 154B Vapor Fractometer with column W (polyethylene glycol on powdered Teflon) at 80° and helium as the carrier gas.

In the first experiment an ampoule containing 10 ml. of a 0.1 *M* solution of benzyldimethyl-*p*-toluidinium bromide in ethanol was kept at 71.7 ± 0.1° for about 16 half-lives. The contents were distilled at atmospheric pressure, and a forerun of 2.5 ml. was collected and analyzed by vapor phase chromatography. The products found included ethyl bromide (4% of the 10 ml.) and ethyl ether (15%). Neither of these products was detected in the 7.5-ml. residue.

The above experiment was repeated under conditions which simulated an actual rate measurement. Ampoules were removed at appropriate times and 3.0-ml. foreruns were distilled at atmospheric pressure. These were again analyzed by v.p.c. It was found that ethyl bromide could first be detected when the extent of solvolysis had attained 60% and that its concentration increased steadily with time. After 143 hours of reaction, a 2% yield of ethyl bromide was present.

Results

The results of measurements of the rates of solvolysis of benzyldimethyl-*p*-toluidinium bromide in absolute ethanol at both 50.8 ± 0.1° and 71.7 ± 0.1° are given in Table I. In all runs but the first, the reaction was followed to beyond 75% completion. All of the runs gave good first-order plots with the exception that a falling off of rate was detectable in the later stages of the reaction, first becoming evident in the range 60–70%

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[1] S. D. Ross, M. Finkelstein and R. C. Petersen, *J. Am. Chem. Soc.*, **82**, 5335 (1960).

of completion. As will be shown later, this divergence from first-order behavior is at least partly due to the incursion of an additional reaction which consumes acid. These late points were not used in calculating the first-order rate constants, k^*, shown in Table I, and in the fourth column, headed "React., %," the highest conversion point used in the calculation of the rate constant has been indicated.

TABLE I

RATES OF REACTION OF BENZYLDIMETHYL-*p*-TOLUIDINIUM BROMIDE IN ETHANOL

Concn., mole/l.	Temp., °C.	$k^* \times 10^6$, sec.$^{-1}$	React., %	Analytical method
0.04957	50.8	0.304	49	Indicator
.02567	50.8	.295	60	Indicator
.10145	50.8	.320	70	Indicator
.09928	71.7	5.28	70	*p*H titration
.02527	71.7	5.07	60	*p*H titration
.04959	71.7	5.47	75	*p*H titration
.09918	71.7	5.27	73	*p*H titration
.09934	71.7	5.46	78	Indicator

The second-order rate constants k_{-1} for the reaction in absolute ethanol at 50.8° between N,N-dimethyl-*p*-toluidine and benzyl bromide to form benzyldimethyl-*p*-toluidinium bromide are listed in Table II. These data were obtained in each case from measurements extending to almost 90% reaction. The average of the values for the rate constant given in Table II is 5.86×10^{-3} l./mole-sec., and the average deviation from this value is 9.3%.

TABLE II

RATES OF REACTION OF N,N-DIMETHYL-*p*-TOLUIDINE AND BENZYL BROMIDE IN ABSOLUTE ETHANOL AT 50.8 ± 0.1°

Bromide, mole/l.	Amine, mole/l.	$k_{-1} \times 10^3$, l./mole-sec.
0.0418	0.1331	5.13
.0410	.1366	5.25
.0403	.1326	6.28
.1352	.0423	6.20
.0698	.0969	6.45

The first-order rate constant for the ethanolysis of benzyl bromide at 50.8° was previously reported[1] to be 8.57×10^{-6} sec.$^{-1}$, having been calculated from the data of three runs which were followed to only 20% of completion. Measurements at higher percentage reaction were vitiated by a side reaction or the reverse reaction which consumed acid.

By vapor phase chromatography, it was shown that both ethyl bromide and diethyl ether are formed in the solvolysis of benzyldimethyl-*p*-toluidinium bromide in ethanol at 71.7°. Ethyl bromide is formed under these conditions in spite of the fact that dimethyl-*p*-toluidine is always present in the reaction mixture in an amount at least as great as the hydrogen bromide. The ether undoubtedly results from alcoholysis of ethyl bromide. To the extent that ethyl bromide is present at any time, the measured conversion of the quaternary ammonium salt is less than the amount actually converted. Table III presents the data obtained from vapor phase chromatographic analysis of the reacting solution during the later stages of the reaction.

TABLE III

FORMATION OF ETHYL BROMIDE AND DIETHYL ETHER IN THE SOLVOLYSIS OF 0.100 *M* BENZYLDIMETHYL-*p*-TOLUIDINIUM BROMIDE IN ABSOLUTE ETHANOL AT 71.7 ± 0.1°

Time, hr.	% solvolysis by acidimetry	Ethyl bromide, mmoles/l.	Diethyl ether, mmoles/l.
24	38	0	0
48	60	0.32	0.05
64	70	.62	.13
72	73	.68	.18
96	82	1.24	.29
115	85	1.47	.55
143		2.01	.95
429		3.60	7.28

Discussion

The decomposition of benzyldimethyl-*p*-toluidinium bromide in refluxing ethanol has been shown to give high yields of benzyl ethyl ether and N,N-dimethyl-*p*-toluidine. The rate of this solvolysis was measured at 50.8 and 71.7° and was found to be first order in the quaternary ammonium salt concentration. The first-order rate constants show little or no dependence on initial salt concentration (Table I), but the rate appears to decrease in the later part of the reaction. This decrease could reasonably be attributed to experimental errors whose effect becomes most noticeable as the reaction approaches completion; but in addition to this possibility, the formation of ethyl bromide (Table III) was sufficient to account for a substantial portion of the apparent decrease in rate.

To rationalize the observed kinetic behavior, the following series of reactions is proposed

$$\mathrm{Q^+ + Br^+ \xrightleftharpoons{K} I} \tag{1}$$

$$\mathrm{I \xrightleftharpoons[k_{-1}]{k_1} C_6H_5CH_2Br + B} \tag{2}$$

$$\mathrm{C_6H_5CH_2Br \xrightarrow[EtOH]{k_2} C_6H_5CH_2OEt + HBr} \tag{3}$$

$$\mathrm{HBr + B \xrightleftharpoons{K'} BH^+ + Br^- \xrightleftharpoons{K''} [BH^+Br^-]} \tag{4}$$

where Q^+ represents the benzyldimethyl-*p*-toluidinium ion, I represents the ion pair $[Q^+Br^-]$, K is the equilibrium constant for this ion pair formation, B is N,N-dimethyl-*p*-toluidine, $[BH^+Br^-]$ is the N,N-dimethyl-*p*-toluidinium bromide ion pair and K' and K'' are equilibrium constants for their respective equilibria.

Letting P represent the measured product, P is equal to the concentration of benzyl ethyl ether which in turn is equal to the sum of the concentrations of the three acidic products: HBr, BH^+ and $[BH^+Br^-]$. The rate equation is then

$$\mathrm{d}P/\mathrm{d}t = k_2(\mathrm{C_6H_5CH_2Br}) \tag{5}$$

and applying the steady-state approximation to benzyl bromide,

$$\mathrm{d(C_6H_5CH_2Br)}/\mathrm{d}t = 0 = k_1(\mathrm{I}) - k_{-1}(\mathrm{C_6H_5CH_2Br})(\mathrm{B}) - k_2(\mathrm{C_6H_5CH_2Br}) \tag{6}$$

If it is then assumed that the equilibrium represented by K' lies essentially all the way to the right, as it almost certainly does, (B) = ($\mathrm{C_6H_5CH_2Br}$) and

$$k_1(\mathrm{I}) - k_{-1}(\mathrm{C_6H_5CH_2Br})^2 - k_2(\mathrm{C_6H_5CH_2Br}) = 0 \tag{7}$$

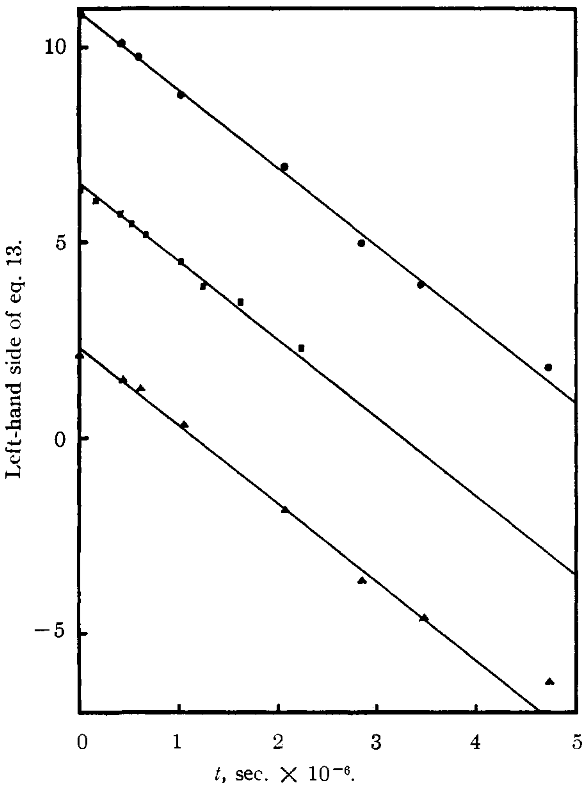

Fig. 1.—Plot of eq. 13 for ethanolysis of N-benzyl-N,N-dimethyl-*p*-toluidinium bromide at 50.8°. Initial salt concentrations: ●, 0.10145 *M;* ■, 0.04957 *M;* ▲, 0.02495 *M.* Lines are drawn with slope of -2.00×10^{-6} sec.$^{-1}$, the negative of the value of k_1 assumed for calculation of the left-hand side of the equation.

Solving eq. 7 for ($C_6H_5CH_2Br$) and substituting the result into eq. 5 yields the rate equation

$$\frac{\mathrm{d}P}{\mathrm{d}t} = -\frac{k_2^2}{2k_{-1}}\left[1 - \sqrt{1 + 4\frac{k_1k_{-1}}{k_2^2}(\mathrm{I})}\right] \qquad (8)$$

Since the reaction was apparently first order in quaternary ammonium salt, eq. 8 was approximated in a manner which would yield a first-order rate expression. It was first assumed that the salt was present almost entirely in the form of ion pairs, in which case (I) = (S) = (S_0 − P) where (S) is the total concentration of quaternary ammonium salt and subscript zero indicates initial conditions ($t = 0$). Then, if k_2^2 is sufficiently greater than $4k_1k_{-1}(\mathrm{I})$

$$\sqrt{1 + 4\frac{k_1k_{-1}}{k_2^2}(\mathrm{I})} = 1 + 2\frac{k_1k_{-1}}{k_2^2}(\mathrm{I}) \qquad (9)$$

and

$$\mathrm{d}P/\mathrm{d}t = k_1(\mathrm{I}) = k_1(\mathrm{S}_0 - \mathrm{P}) \qquad (10)$$

Equation 10 represents the observed first-order behavior and states further that the observed overall rate constant k^* is just the rate constant k_1 for conversion of the ion pair to benzyl bromide plus amine. The validity of the approximation implied by eq. 9 can now be tested with the aid of the independently determined values of k_{-1} and k_2. With $k_1 = k^* = 3 \times 10^{-7}$ sec.$^{-1}$ (Table I), $k_{-1} = 5.9 \times 10^{-3}$ l./mole-sec. (Table II), $k_2 = 8.6 \times 10^{-6}$ sec.$^{-1}$ (previously reported[1]) and with salt concentration variant in the approximate range 0.01 – 0.10 *M*, k_2^2 is about 7×10^{-11} while $4k_1k_{-1}$ (I) varies from about 7×10^{-11} to 7×10^{-10} sec.$^{-2}$. Thus the approximation is not valid and eqs. 9 and 10 must be rejected.

Equation 8 was next integrated without the aid of this approximation with the result

$$\sqrt{1 + k(\mathrm{S}_0 - \mathrm{P})} + \ln\left(\sqrt{1 + k(\mathrm{S}_0 - \mathrm{P})} - 1\right) = \sqrt{1 + k(\mathrm{S}_0)} + \ln\left(\sqrt{1 + k(\mathrm{S}_0)} - 1\right) - k_1t \qquad (11)$$

where $k = 4k_1k_{-1}/k_2^2$ and $P = 0$ at $t = 0$. Since k_{-1} and k_2 are known, it should be possible to select a value of k_1 to be used in evaluating k such that when the left-hand side of the equation is plotted *versus* t there will result a straight line of slope ($-k_1$). It developed that this could be done, but that very different values of k_1 were required for runs with different initial salt concentrations. The mechanism represented by eq. 8 combined with the assumption of complete ion pairing is thus not satisfactory.

In the next analysis, the quaternary ammonium salt was permitted to exist as both free ions and ion pairs, but the N,N-dimethyl-*p*-toluidinium salt which is a product of the reaction was assumed to be present entirely in the associated form (K'' infinite). This would not be an abnormal situation, for the center of charge of the ternary ammonium ion would be nearer the surface of the ion than in the quaternary case, thereby promoting association, while the excess bromide ion provided by dissociated quaternary ammonium bromide would serve further to drive this equilibrium toward association. With this less stringent set of assumptions, eq. 7 was again solved and the result was substituted into eq. 5 to yield the differential equation

$$\frac{\mathrm{d}P}{\mathrm{d}t} = -\frac{k_2^2}{2k_{-1}}\left[1 - \sqrt{1 + \alpha(1 - A)^2}\right] \qquad (12)$$

where $\alpha = k_1k_{-1}/Kk_2^2$ and $A = \sqrt{1 + 4K(\mathrm{S}_0 - \mathrm{P})}$. It was not possible by means of simple approximations to convert the right-hand side of eq. 12 to the experimentally observed form $k^*(\mathrm{S}_0 - \mathrm{P})$, so eq. 12 was integrated with the initial condition that $P = 0$ at $t = 0$ with the result

$$\frac{1 + \sqrt{1 + \alpha(1 - A)^2}}{1 - A} - \sqrt{\alpha}\ln\left[\sqrt{\alpha}(1 - A) + \sqrt{1 + \alpha(1 - A)^2}\right] + \sqrt{1 + \alpha(1 - A)^2} + \ln\frac{(1 - A)^2}{1 + \sqrt{1 + \alpha(1 - A)^2}} = \frac{1 + \sqrt{1 + \alpha(1 - A_0)^2}}{1 - A_0} - \sqrt{\alpha}\ln\left[\sqrt{\alpha}(1 - A_0) + \sqrt{1 + \alpha(1 - A_0)^2}\right] + \sqrt{1 + \alpha(1 - A_0)^2} + \ln\frac{(1 - A_0)^2}{1 + \sqrt{1 + \alpha(1 - A_0)^2}} - k_1t \qquad (13)$$

where A_0 is the value of A at $t = 0$ ($P = 0$).

With k_2 and k_{-1} known, eq. 13 was fitted to the data of the three runs at 50.8° by assuming values for K and k_1 and plotting the left-hand side of the equation *versus* t with the requirement for a fit being that the negative of the slope obtained must equal the assumed value of k_1 and that the same value of k_1 must fit all three runs. This fit was achieved with $K = 20$ l./mole and $k_1 = 2.0 \times 10^{-6}$ sec.$^{-1}$ and is illustrated by Fig. 1. The association constant K may be compared with the following values recently computed by Kay[2] for alkali chlorides in ethanol at 25°: LiCl, 27; NaCl, 44; KCl, 95.

Reasonable fits may be obtained with other values of K and k_1 within about 10% of the values used here. The previously described decrease in rate in the late stages of the reaction is just becoming noticeable in Fig. 1; later points, not shown here, deviate still more from the straight lines.

Since a certain latitude in the values of K and k_1 is permissible while retaining a good fit of the data, and since these values further depend on the accuracy of the values used for k_{-1} and k_2 as well as the steady-state approximation and the assumption of complete association of the ternary ammonium salt, these values of K and k_1 must be considered to be only approximate values. It will most certainly be possible to fit the data with finite values of K'', while the degree of validity of the steady-state approximation is always difficult and often impossible to evaluate, but, having obtained a satisfactory fit of the data, further refinement of the analysis is not justified.

It is most interesting to note that, while the value $K = 20$ implies only 15 to 50% association in the range 0.01 to 0.10 M total salt concentration, the rate data for the over-all solvolysis reaction fit first-order kinetics. A simple first-order ethanolysis of the quaternary ammonium ion is ruled improbable by the fact that varying the anion causes a large change in the rate of ethanolysis of benzyldimethylanilinium ion.[1] Another simple formulation which leads to first-order kinetics, based on complete association of all ionic species followed by ethanol attack on the quaternary ammonium bromide ion pair to give final products without the benzyl bromide and amine intermediates, is largely ruled out by the same experimental observation, since in such a case the only significant property of the anion would be its charge. We are thus led to the sequence described by eqs. 1–4 to represent the course of the ethanolysis of benzyldimethyl-*p*-toluidinium bromide.

This reaction may profitably be compared to the decomposition of some ternary sulfonium salts. The rates of reaction of trimethylsulfonium salts have been measured by Gleave, Hughes and Ingold[3] who conclude that the rates of decomposition of the carbonate, bromide and chloride in ethanol are identical. In the light of more recent work by Swain and Kaiser,[4] this conclusion was re-examined by Hughes, Ingold and Pocker[5] who presented new data with the conclusion that there exists a substantial difference between the rates of decomposition of trimethylsulfonium chloride and bromide. Assuming more credence can be attached to the later work, the observation accords with the similar observation in the case of ethanolysis of certain quaternary ammonium salts.

The decomposition of various trimethylsulfonium[3–5] and tribenzylsulfonium[4] salts has also been shown to be apparently first order in total salt concentration. These sulfonium halide decompositions are somewhat simpler than the case of the quaternary ammonium solvolyses discussed here, since the reaction whose rate is measured is conversion of the salt to dimethyl (or dibenzyl) sulfide plus methyl (or benzyl) halide. The reactions analogous to those represented by k_{-1}, k_2, K' and K'' of eqs. 1–4 can thus be eliminated from a discussion of the sulfonium cases.

Swain and Kaiser,[4] in their study of the decomposition of tribenzyl- and trimethylsulfonium chlorides in 90% aqueous acetone, recognized that the apparent first-order behavior could be explained by the existence of a substantial degree of ionic association, but they discarded this possibility on the basis of some insufficiently precise conductivity measurements. More refined conductivity work by Jacobson and Hyne[6] on trimethylsulfonium iodide in ethanol–water mixtures suggests that these systems are, in fact, highly associated and the rejection of the ion-pair formulation by Swain and Kaiser was not justified.

The ethanolysis of benzyldimethyl-*p*-toluidinium bromide presents a clear, albeit not ideally simple, demonstration of the utility and validity of the ion-pair concept in describing the course of organic ionic reactions, while it appears that the reaction of benzyldimethylanilinium ion with ethoxide ion in ethanol[1] and with thiocyanate ion in various solvents,[7] as well as the decomposition of certain sulfonium salts in selected solvents,[3–6] can also be discussed most reasonably in these same terms.

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[2] R. L. Kay, *J. Am. Chem. Soc.*, **82**, 2099 (1960).

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[5] E. D. Hughes, C. K. Ingold and Y. Pocker, *Chemistry & Industry*, 1282 (1959).

[6] A. L. Jacobson and J. B. Hyne, *J. Am. Chem. Soc.*, **82**, 2418 (1960).

[7] S. D. Ross, M. Finkelstein and R. C. Petersen, *ibid.*, **83**, 4853 (1961).