THE MECHANISM OF THE CARBONYL ELIMINATION REACTION OF BENZYL NITRATE

KINETIC ISOTOPE EFFECTS AND DEUTERIUM EXCHANGE¹

ERWIN BUNCEL² AND A. N. BOURNS

ABSTRACT

The carbonyl elimination reaction $(E_{\rm CO}2)$ of benzyl nitrate has been investigated with the object of distinguishing between the concerted and carbanion mechanisms. A deuterium exchange experiment resulted in a very small amount of deuterium pickup. The nitrogen isotope effect, k_{14}/k_{15} , associated with formation of the nitrite ion was found to be 1.0196 ± 0.0007 at 30° C. The two results taken together exclude the formation of a carbanion intermediate but are consistent with a concerted mechanism.

Benzyl- α - d_2 nitrate has been prepared and the rate of its carbonyl elimination reaction compared with that of the undeuterated compound. The deuterium isotope effect was 5.04 ± 0.25 at 60° C. The significance of the magnitude of the nitrogen and deuterium isotope effects and of their interrelationship with the Hammett reaction constant *rho* is discussed in terms of the nature of the transition state and a comparison is made with other E2 elimination reactions.

Nitrate esters have been extensively studied during the last decade and are the subject of a recent review article (1). Several types of reaction have been observed with nucleophilic reagents (2, 3). The reaction followed in a given system depends on the structure of the nitrate, the nature of the nucleophilic reagent, and the solvent, and often two or more of the reactions take place simultaneously.

1. Substitution on carbon:

2. Substitution on nitrogen:

$$RCH_2 - CH_2 - O - NO_2 + Y - - - RCH_2CH_2O^- + Y - - NO_2$$
.

3. β -Hydrogen elimination:

$$\operatorname{RCH}_2$$
--CH₂-O-NO₂ + Y⁻----> RCH_2 -CH₂ + NO₃⁻ + YH.

4. α -Hydrogen elimination:

 $RCH_2 - CH_2 - O - NO_2 + Y^- - \rightarrow RCH_2CH = O + NO_2^- + YH.$

The substitution reaction on carbon has been shown (2) to follow either the S_N1 or the S_N2 mechanism, the factors determining the course of reaction being analogous to those for alkyl halides. For example, in 90% ethanol the rate of reaction of *tert*-butyl nitrate is first order, being independent of the hydroxide ion concentration, while for ethyl nitrate the rate is second order, being proportional to both the nitrate and the hydroxide ion concentrations. Evidence for substitution on nitrogen (reaction 2) is based on oxygen-18 studies of the position of bond fission in the hydrolysis of *n*-butyl and *n*-octyl nitrate (4) and on stereochemical studies in the hydrolysis of optically active 2-octyl nitrate (5). This reaction differs from the others in that it results in the nitration of the base, and this property has been utilized as a synthetic method for the nitration of amines and active methylene groups (6, 7). The β -hydrogen elimination of

¹Manuscript received August 16, 1960.

Contribution from the Burke Chemical Laboratories, Hamilton College, McMaster University, Hamilton, Ontario. ²National Research Council of Canada Postdoctorate Fellow 1958–60.

Can, J. Chem. Vol. 38 (1960)

CANADIAN JOURNAL OF CHEMISTRY, VOL. 38, 1960

alkyl nitrates (reaction 3) has also been shown to proceed by the unimolecular or bimolecular mechanisms (2) and often occurs concurrently with substitution on carbon.

Whereas the first three types of reaction cited have counterparts in the reactions of carboxylic esters or alkyl halides, the α -hydrogen elimination finds no direct analogy in the reactions of these compounds. It has been named a carbonyl elimination reaction (2) and has been designated $E_{\rm Co}2$ since it always shows the characteristics of a typical bimolecular reaction, viz., a strong base is necessary to remove the α -hydrogen atom and the reaction has never been observed under solvolytic conditions. From a thorough study Baker and Heggs concluded that the $E_{\rm Co}2$ reaction is strongly facilitated by increased acidity of the eliminated hydrogen and by substituent groups which can conjugate with the forming carbonyl bond (8). The importance of these factors in determining the rates of the $E_{\rm Co}2$ reaction and the yields of aldehyde product is demonstrated by the following data, obtained in 90% aqueous ethanol at 60° C (8): ethyl nitrate, 0.2×10^{-5} l. mole⁻¹ sec⁻¹, 2%; *p*-methylbenzyl nitrate, 3×10^{-3} l. mole⁻¹ sec⁻¹, 54%; benzyl nitrate, 8×10^{-3} l. mole⁻¹ sec⁻¹, 87%; and *p*-nitrobenzyl nitrate, 3×10^2 l. mole⁻¹ sec⁻¹, 100%. The Hammett reaction constant ρ for *m*- and *p*-substituted benzyl nitrates has the high positive value of +3.40.

By analogy with other elimination reactions, two mechanisms must be considered for the carbonyl elimination reaction of organic nitrates.

Concerted mechanism

$$\begin{array}{c} H \\ C_{6}H_{5} \end{array} CH \rightarrow O \\ NO_{2} \end{array} + C_{2}H_{5}O^{-} \rightarrow \left[\begin{array}{c} \rho \\ OC_{2}H_{5} \\ H \\ C_{6}H_{5} \end{array} \right] \rightarrow C_{6}H_{5}CH = O + NO_{2}^{-}$$

$$\begin{array}{c} 0 \\ C_{6}H_{5} \end{array} CH = O \\ NO_{2} \end{array} \right] \rightarrow C_{6}H_{5}CH = O + NO_{2}^{-}$$

$$\begin{array}{c} 0 \\ C_{6}H_{5} \end{array} CH = O \\ NO_{2} \end{array}$$

transition state

Two-step mechanism

 \cap

$$\begin{array}{cccc} H \\ C_{6}H_{5} \end{array} CH \rightarrow O_{NO_{2}} + C_{2}H_{5}O^{-} & \overleftarrow{k_{1}} \\ \hline k_{2} \end{array} \xrightarrow{\ominus} C_{6}H_{5} \xrightarrow{\ominus} CH \rightarrow O_{NO_{2}} + C_{2}H_{5}OH$$
[2]

$$C_6H_5$$
 $C_6H_5CH=0 + NO_2^-$ [3]

In the concerted mechanism the removal of hydrogen by base is synchronous with formation of the carbon-oxygen double bond and separation of nitrite ion. This is analogous to the E2 mechanism observed in olefin-forming eliminations of alkyl halides, ammonium and sulphonium salts (9). The alternative possibility is a two-step process in which the base first removes the hydrogen to form a carbanion intermediate which subsequently eliminates the nitrite ion with formation of aldehyde. This corresponds to the E1cb mechanism suggested by Ingold as a possible path in olefin-forming eliminations, and may be designated $E_{co}1cb$ (8). Cristol has proposed that the E1cb mechanism does indeed occur in cyclic systems where the eliminated groups have cis orientations (10, 11).

The carbonyl elimination reaction is one in which the carbanion mechanism is expected to be "inherently probable" (8), and a particularly favorable system should be that of

2458

BUNCEL AND BOURNS: CARBONYL ELIMINATION REACTION

benzyl nitrate. The high positive value for the Hammett reaction constant ρ , +3.40, obtained for *m*- and *p*-substituted benzyl nitrates, and the fact that the σ^* value (12) for the para-nitro group must be used for a linear relationship to hold between log *k* and σ clearly show that the transition state of the reaction has a high degree of carbanion character. Further, the strongly electron-attracting nitrate group will have an appreciable effect on the acidity of the eliminated hydrogen, and this would be expected to promote reaction by a carbanion mechanism.³

The present investigation was undertaken with the object of establishing which of the two possible mechanisms, the concerted or the two-step, is being followed in the carbonyl elimination reaction of benzyl nitrate.

Deuterium Exchange Test

An established method for detecting a carbanion intermediate in an elimination reaction is the deuterium exchange test of Skell and Hauser (14). The reaction between substrate and base is carried out in hydroxyl-deuterated solvent (the solvent being the conjugate acid of the base) to partial completion and the unreacted substrate is isolated and examined for its deuterium content. If a true carbanion intermediate is present then the reverse of the first stage will result in deuterium pickup by the substrate.

An appreciable pickup of deuterium by the substrate would unquestionably prove that a carbanion intermediate is formed. The absence of deuterium pickup, however, would not necessarily exclude the intervention of a carbanion intermediate, since the rate at which the carbanion decomposes to product could be so much greater than its rate of return to reactant by combination with solvent (i.e., $k_3 \gg k_2$) as to preclude the observation of deuterium in the recovered substrate by the available experimental methods.

A deuterium exchange test was carried out with benzyl nitrate and ethoxide ion in anhydrous 99% ethanol-1-d. The reaction was interrupted at about 40% completion by the addition of p-toluenesulphonic acid. The unchanged benzyl nitrate was recovered and purified by fractional distillation. It was analyzed for deuterium by combustion to water and measurement of the O-D absorption at 2500 cm⁻¹ (15). The purest sample of benzyl nitrate isolated, as judged by the identity of its infrared spectrum with authentic benzyl nitrate, analyzed for a deuterium content of 0.007 ± 0.003 atom% excess of deuterium. The significance of such a small deuterium content is open to more than one explanation. It could result from the actual presence of C₆H₅CHDONO₂ (0.05 mole% excess) formed by the reaction of a carbanion intermediate with deutero-ethanol. In this case the observed deuterium enrichment would require that for every one carbanion that reverts to reactant 1200 decompose to product (see Experimental), i.e., $k_3/k_2 = 1200$, where k_3 includes the concentration of solvent deutero-ethanol.⁴ An alternative explanation, however, is that this very small deuterium enrichment is caused by the presence of some deuterium-containing contaminant.⁵

In past studies of elimination reactions the interpretation given to the observation of a very small deuterium enrichment in the recovered reactant has varied. Some workers

³Cristol found that in a cis dehydrochlorination the replacement of a chlorine substituent by the strongly electronattracting p-toluenesulphonyl group increased the rate of reaction by a factor of about 10¹⁰ (13). ⁴Because of a possible isotope effect associated with the reaction of deutero-ethanol with carbanion, the k_3/k_2

ratio in undeuterated ethanol may differ somewhat from this figure (16).

⁵Some enrichment will undoubledly arise from a kinetic isotope effect involving the reactant, which originally has the natural isotopic abundance of deuterium. It can be shown, however, that this factor could account for no more than a quarter of the observed enrichment.

CANADIAN JOURNAL OF CHEMISTRY. VOL. 38, 1960

have taken the result to mean the absence of exchange and have inferred that a concerted mechanism is being followed (14), while others have concluded that the enrichment is evidence in support of a carbanion intermediate (10).

Kinetic Nitrogen Isotope Effect

2460

In previous applications of the deuterium exchange test the ambiguity presented by an apparent very small deuterium pickup could not be resolved. It has been possible to resolve this problem in the present reaction system by an evaluation of the kinetic nitrogen isotope effect. In the concerted process (equation [1]) the O—NO₂ bond is broken in the rate-determining step and this should result in a nitrogen isotope effect of considerable magnitude, i.e., of the order of 1-3% (vide infra). In the carbanion mechanism with $k_3 \gg k_2$, which is the only possibility for a carbanion mechanism permitted by the results of the deuterium study, the rate-determining step is the formation of the carbanion in which the bonds associated with nitrogen are still intact. In this case there should be no nitrogen isotope effect, or at the most an isotope effect of a few tenths of a per cent.

A kinetic nitrogen isotope effect study was undertaken with benzyl nitrate of normal isotopic composition. The procedure consisted of allowing reaction between benzyl nitrate and ethoxide ion to proceed to 10% completion and comparing the nitrogen isotopic composition of the formed nitrite ion with that of the starting benzyl nitrate. Since a simultaneous substitution reaction results in displacement of nitrate ion, a separation of the nitrate ion formed in the carbonyl elimination reaction was required.⁶ This separation was achieved by selective reduction of the nitrite and nitrate ion to ammonia (17). The ammonia was subsequently oxidized to nitrogen (18), which was analyzed by mass spectrometry. The total nitrite and nitrate ion obtained from the 100% reaction was similarly converted to nitrogen and analyzed by mass spectrometry. The results of these experiments are shown in Table I.

TABLE I

Expt. No.	Extent of reaction	N^{14}/N^{15}	
		$NO_2^- + NO_3^-$	NO ₂ -
1	100	265.58	
2	100	265.78	
3	100	265.46	
4	100	265.66	
5	100	265.62	
6	10		270.52
7	10		270.54
8	10		270.66
9	10		270.42
10	10		270.74
Mean N14/N15 ratios*		$265.62 \pm .12$	$270.58 \pm$

*The limits shown are the standard deviations.

The kinetic isotope effect, calculated from these isotopic ratios and the known extent of reaction (19), is

$k^{14}/k^{15} = 1.0196 \pm 0.0007.$

⁶Experiments using nitrogen-15 enriched nitrate ion established the absence of isotopic exchange between nitrite and nitrate ions under the reaction conditions and in the subsequent separation procedure. Details of this work will be published elsewhere.

This isotope effect, which is one of the largest observed for nitrogen in a rate process unequivocally establishes that the O—N bond is undergoing rupture in the rate-determining step. Since the observation of no significant deuterium exchange has ruled out a carbanion mechanism in which the step involving O-N bond rupture is rate determining, it follows that only a concerted process is consistent with the results of both the nitrogen isotope effect and the deuterium exchange studies.

Although the results of this investigation clearly exclude the carbanion mechanism for the reaction of benzyl nitrate the possibility still exists for reaction by this mechanism with reactants in which structural features would provide greater stability to a carbanion. Systems of this type are under investigation.

It was convenient to determine the nitrogen isotope effect in the competing substitution reaction forming nitrate ion since this had been converted to ammonia in the process of separating it from the elimination product. The isotopic ratio for the nitrogen of nitrate ion (combined products of experiments 6-10) was 265.52, which is identical, within the limit of measurement, with the mean value obtained for the product of 100%reaction. This observation of a zero isotope effect is consistent with a nucleophilic substitution of ethoxide ion on carbon with displacement of nitrate ion.

Hydrogen-Deuterium Isotope Effect

To gain greater insight into the nature of the transition state of the carbonyl elimination reaction the hydrogen-deuterium isotope effect for the reaction has also been determined. This was measured by separately evaluating the specific reaction constants for $C_6H_5CH_2ONO_2$ and $C_6H_5CD_2ONO_2$. Benzyl- α -d₂ nitrate was prepared by the lithium aluminum deuteride reduction of ethyl benzoate to benzyl- α - d_2 alcohol which was converted to benzyl- α -d₂ chloride and to benzyl- α -d₂ nitrate by usual procedures. The kinetics were conducted in anhydrous ethanol. The total rate was followed by acid-base titration and the rate constants for the carbonyl elimination reaction, $k_{E_{CO}2}$, and for the substitution reaction, $k_{S_N^2}$, were evaluated from the relative yields of nitrite and nitrate ions. These yields remained constant throughout the reaction, demonstrating that the two ions were formed by reactions of the same kinetic order. The rate data are shown in Table II. It is seen that the carbonyl elimination reaction shows an isotope effect of 5.0 at 60° C. From the data given in Table II one may also calculate a $k_{\rm H}/k_{\rm D}$

TABLE II							
Hydrogen-deuterium isotope effect at 60.2° C							

	$C_6H_5CH_2ONO_2$	C ₆ H ₅ CD ₂ ONO ₂
$\% E_{\rm CO2}$	88.7	64.4
$\% S_{\rm N}2$	11.3	35.6
$10^3 k_{total}^*$	13.9	3.79
$10^{3} k_{ECO^{2}}$	12.3	2.44
$10^{3} k_{SN^{2}}$	1.57	1.35

*k in 1. mole⁻¹ sec⁻¹.

Testimated uncertainty based upon variation in yields of nitrite ion and rate constant values.

ratio of 1.16 for the substitution reaction. No significance, however, is attached to the difference between this value and unity because of the rather large percentage error in the determination of the small amount of nitrate ion.

Nature of the Transition State in the E_{co} 2 Reaction

Information concerning charge distribution and extent of bond rupture in the transition state of a bimolecular elimination reaction of the type

$$Z - C_{6}H_{4} - CH - Y - X \xrightarrow{B^{-}} \begin{bmatrix} \delta^{-} & \delta^{-} \\ Z = -C_{6}H_{4} = -CH = -Y \\ H \end{bmatrix} \rightarrow Z - C_{6}H_{4}CH = Y + BH + X^{-}$$
[4]

transition state

is provided by three quantities: (a) the deuterium isotope effect, (b) the isotope effect associated with the leaving group X, and (c) the Hammett ρ value. A large $k_{\rm H}/k_{\rm D}$ value implies a large degree of carbon-hydrogen bond stretching with the release to the rest of the molecule of the electron pair associated with this bond. The resulting negative charge may reside largely on the carbon atom and its attached aryl group, in which case the transition state may be described as having a high degree of carbanion character and the reaction will be characterized by a large positive Hammett ρ , or the charge may reside in part or in whole on the leaving group X. Other factors being equal, the greater the extent to which this charge is accommodated in the transition state by the leaving group the more highly concerted the reaction, the larger the isotope effect associated with X, and the smaller the ρ value.

The $k_{\rm H}/k_{\rm D}$ value of 5.0 at 60° C for the $E_{\rm CO}2$ reaction of benzyl nitrate (X = NO₂, Y = O, and Z = H in equation [4]) is large, being only slightly smaller than that calculated (ca. 5.6) for the complete loss of the carbon-hydrogen bond stretching frequency in the transition state (16). The ρ value, +3.4, for the $E_{\rm CO}2$ reaction of substituted benzyl nitrates is large also; indeed, it is larger than the ρ values observed in other bimolecular elimination reactions involving ethoxide ion (20), and is one of the largest found for a rate process (12). To a considerable extent, then, the negative charge which is developed as a result of the large carbon-hydrogen bond stretching resides on the benzyl carbon, and the transition state, therefore, may be described as having a high degree of carbanion character.

That the oxygen-nitrogen bond is also considerably weakened in the transition state of the $E_{co}2$ reaction of benzyl nitrate is evident from the magnitude of the nitrogen isotope effect, 2.0% at 30° C. Although this value is considerably smaller than the 3.8%⁷ calculated on the assumption of complete oxygen-nitrogen bond rupture in the transition state, it is significantly greater than the nitrogen isotope effect of 1.3% found in this laboratory (24) for the E2 Hofmann elimination reaction of β -phenylethyltrimethylammonium bromide (X = $\mathring{N}(CH_3)_3$, Y = CH₂, and Z = H in equation [4]) with

methylammonium bromide (X = N(CH₃)₃, Y = CH₂, and Z = H in equation [4]) with ethoxide ion at the same temperature. Since the deuterium effect is also larger, 5.0 at 60° C compared with 3.0 at 50° C observed by Saunders for the Hofmann reaction (25), it would appear that rupture of both C—H and Y—X bonds is more fully developed in the transition state of the carbonyl elimination reaction. On the other hand, the transition state for the $E_{\rm CO}2$ reaction must have considerably more carbanion character than that of the bimolecular elimination with ethoxide ion of the structurally related β -phenylethyl bromide (X = Br, Y = CH₂, and Z = H in equation [4]). The deuterium

⁷This value is obtained from the Bigeleisen expression (21) using 860.6 cm⁻¹ for the stretching vibration of the O—NO₂ bond (22) in evaluating the free-energy term and the Slater theorem for the effective mass term. Using the mass fragment method of evaluating the mass term (23), the calculated effect is 2.8%.

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 8.26.113.34 on 11/19/14 For personal use only.

BUNCEL AND BOURNS: CARBONYL ELIMINATION REACTION

isotope effect for this dehydrobromination reaction has the abnormally large value of 7.1 at 30° C (25), while the ρ value for the reaction of substituted β -phenylethyl bromides is only +2.18 (20), compared with the +3.4 found for the $E_{co}2$ reaction of the benzyl nitrates. More of the negative charge developed in the transition state must, therefore, reside on the bromine atom in the halide reaction than on the nitro group in the carbonyl elimination, and carbon-bromine bond rupture must have progressed further than oxygen-nitrogen bond rupture.

From these considerations it would appear that with respect to the extent to which bonds have been weakened, the transition state for the carbonyl elimination of benzyl nitrate is intermediate between the transition states for the E2 reaction of β -phenylethyltrimethylammonium ion and of β -phenylethylbromide.

EXPERIMENTAL

Materials

Benzyl nitrate.—This was prepared from benzyl chloride and silver nitrate in acetonitrile (26). The product, purified by fractional distillation from silver nitrate and calcium carbonate, was obtained in 75% yield (b.p. $45^{\circ}/0.5 \text{ mm}$, $n_{\rm D}^{20}$ 1.5209).

Benzyl- α - d_2 nitrate.—The steps involved in the synthesis of benzyl- α - d_2 nitrate were: (1) reduction of ethyl benzoate to benzyl- α - d_2 alcohol with lithium aluminum deuteride; (2) conversion of benzyl- α - d_2 alcohol to benzyl- α - d_2 chloride with zinc chloride and hydrochloric acid; and (3) reaction of benzyl- α - d_2 chloride with silver nitrate in acetonitrile. The over-all yield of benzyl- α - d_2 nitrate (b.p. 45°/0.5 mm, n_D^{20} 1.5203) was 62%. A N.M.R. analysis⁸ showed that the product was 99% C₆H₅CD₂ONO₂.

Benzyl- α - d_2 alcohol.—Ethyl benzoate (28.5 g, 0.190 mole) was reacted for 4 hours with lithium aluminum deuteride (3.94 g, 0.099 mole) in 400 ml ether which had been distilled from lithium aluminum hydride, and the complex was then decomposed with 10% sulphuric acid. The product, recovered by ether extraction, was treated with aqueous alcoholic sodium hydroxide to hydrolyze any unreacted ethyl benzoate. After removal of ethanol and extraction with ether, distillation yielded benzyl- α - d_2 alcohol (b.p. 76°/5 mm, n_{20}^{20} 1.5398) in 84% yield.

Benzyl- α - d_2 chloride.—Benzyl- α - d_2 alcohol (17.4 g, 0.158 mole) was added during 1 hour to 77 g of a stirred solution of hydrochloric acid and zinc chloride (Lucas' reagent (27)) at 0° C. Stirring was continued for 1 hour at 0° C and 2 hours at room temperature. The reaction mixture separated into two layers and was extracted with a 1:1 mixture of ether and petroleum ether. Distillation yielded benzyl- α - d_2 chloride (b.p. 64°/12 mm) in 86% yield.

Deuterium Exchange Experiment

Ethanol-1-d was prepared by the action of 99.4% deuterium oxide on sodium ethoxide, prepared from molecular sodium (28) under strictly anhydrous conditions in a nitrogen atmosphere. The product was shown by N.M.R.⁸ to be at least 99% deuterated on the hydroxyl group. A solution of sodium ethoxide in the deutero-ethanol (ca. 0.5 *M*) was prepared by dissolution of sodium metal and was standardized by titration with acid. Fifty milliliters of the ethoxide solution was added to an equimolar quantity of benzyl nitrate and reaction was allowed to proceed at 30° C to an appropriate extent of completion when it was quenched by addition of *p*-toluenesulphonic acid. Solvent was removed under reduced pressure and the residue was taken up in ether and washed

⁸N.M.R. analyses were performed by Dr. R. J. Gillespie.

CANADIAN JOURNAL OF CHEMISTRY, VOL. 38, 1960

with ice-cold water. The extent of reaction was determined by an acid-base titration of the aqueous washings. The ethereal solution was evaporated and treated with three 25-ml quantities of methanol, each of which was removed by distillation through a Vigreux column. The purpose of this methanol treatment was to remove last traces of deutero-ethanol and to exchange any hydroxyl-deuterated benzyl alcohol which may have been formed by hydrolysis following the quenching. The product of this treatment was fractionally distilled through a 15-cm tantalum spiral column. Deuterium analysis was carried out by combustion of the recovered benzyl nitrate and measurement of the O-D absorption at 2500 cm⁻¹ in the water formed (15).

In the first exchange experiment, carried to 44% completion, two fractions of benzyl nitrate were collected, both of which showed some contamination with benzaldehyde, as shown by a carbonyl absorption in the infrared spectra, although the higher boiling fraction was the purer. The analysis results for the two fractions were 0.029 ± 0.006 and 0.015 ± 0.003 atom% excess deuterium, respectively. In a second exchange experiment, carried to 37% completion, the recovered material was more carefully purified and a fraction which was almost completely carbonyl-free was obtained. This fraction was found to contain 0.007 ± 0.003 atom% excess deuterium.

On the basis of the carbanion intermediate mechanism one can calculate the k_3/k_2 ratio corresponding to a deuterium pickup of 0.007 atom%. Assuming that only one hydrogen in the benzyl nitrate exchanges, the following can be derived from equations [2] and [3]. (The rate constant for the reverse step in equation [2] will here also be denoted by k_2 even though it now applies to the reaction of carbanion with deutero-ethanol.)

$$\frac{d}{dt} \left[C_6 H_5 CHDONO_2 \right] = k_2 \left[C_6 H_5 CHONO_2 \right] \left[C_2 H_5 OD \right]$$
[5]

$$\frac{d}{dt} [\text{product}] = k_3 [C_6 H_5 CHONO_2]$$
[6]

Dividing equations [5] and [6] and integrating one obtains

$$\frac{[C_{6}H_{5}CHDONO_{2}]}{[C_{6}H_{5}CHDONO_{2}] + [C_{6}H_{5}CH_{2}ONO_{2}]} = \frac{k_{2}[C_{2}H_{5}OD]}{k_{3}}$$
[7]

 $\times \frac{[\text{product}]}{[C_6H_5CHDONO_2] + [C_6H_5CH_2ONO_2]}$

Substituting $[(0.007 \times 7)/100] = 0.00049$ for the mole fraction excess of C₆H₅CHDONO₂ in the benzyl nitrate recovered after 37% reaction, it follows that

$$\frac{k_3}{k_2[C_2H_5OD]} = \frac{37}{63 \times 0.00049} = 1200.$$

Kinetic Measurements with C₆H₅CH₂ONO₂ and C₆H₅CD₂ONO₂

A solution of benzyl nitrate (0.04-0.05 M) and sodium ethoxide (0.05-0.08 M) in anhydrous ethanol was prepared by the addition of standard sodium ethoxide solution to a weighed amount of the nitrate and was maintained in a constant temperature bath to $\pm 0.03^{\circ}$ C. At suitable intervals of time aliquots of 2 ml each were removed and added to 15 ml of ice-cold water for quenching the reaction. Following titration with standard acid the unreacted nitrate ester was extracted with petroleum ether. The aqueous extract was analyzed for nitrite and nitrate ions by a modification of the method described by Varner *et al.* (17). This method is based on the differential rates of reduction

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 8.26.113.34 on 11/19/14 For personal use only. 2464

BUNCEL AND BOURNS: CARBONYL ELIMINATION REACTION

2465

of nitrite and nitrate to ammonia. While nitrite ion is rapidly reduced by ferrous hydroxide alone, the presence of a silver ion catalyst is required for the reduction of nitrate ion.

The solution containing nitrite and nitrate was placed in a Kjeldahl-type distillation apparatus constructed with a double splash-head. A 40% aqueous sodium hydroxide solution (15 ml) was added and steam was passed through until all the ethanol had distilled over. This initial removal of ethanol was found to be necessary for quantitative reduction. A 20% aqueous solution of ferrous sulphate (5 ml) was added and steam distillation continued for 3 minutes during which time the nitrite ion was reduced to ammonia which was collected in 5% boric acid solution. The nitrate ion was then reduced on the addition of a saturated silver sulphate solution (5 ml) and the ammonia formed was distilled during 5 minutes into a fresh receiver containing boric acid solution. The ammonia from the reductions was titrated with 0.01 N sulphuric acid using methyl red-methylene blue indicator. A complete analysis involving the reduction of both nitrite and nitrate was performed without interruption of steam distillation.

The over-all rate constant for the reaction was calculated from the usual second-order plot using the data from the acid-base titrations. At least two kinetic runs were performed with each compound at a given temperature, and rate constants agreed within $\pm 2\%$. The nitrite and nitrate analyses were performed for at least five points in each kinetic run. The yields of nitrite and nitrate ion were reproducible within $\pm 1\%$ absolute and the mean values were used to calculate the rate constants of the component $E_{co}2$ and $S_{N}2$ reactions.

Nitrogen Isotope Effect

Can. J. Chem. Downloaded from www.nrcresearchpress.com by 8.26.113.34 on 11/19/14 For personal use only.

The kinetic nitrogen isotope effect in the $E_{co}2$ reaction was obtained by comparing the nitrogen isotopic abundance in the nitrite ion formed in reactions carried out to some small known extent of completion with the isotopic abundance in the starting compound. The latter was obtained by measuring the isotopic abundance in the combined nitrite and nitrate ion product formed in reactions allowed to proceed to completion.

Benzvl nitrate (0.05 M) and sodium ethoxide (0.05 M) in 50 ml of anhydrous ethanol were allowed to react at 30° C for a length of time corresponding to 10% reaction. The solution was then added to a mixture of ice-cold petroleum ether and 0.1 N aqueous sodium bicarbonate (5% excess over the remaining ethoxide) and the two layers were separated. The bicarbonate served to neutralize excess ethoxide which otherwise would react with the small amount of benzyl nitrate not removed in the petroleum ether. (Neutralization with 0.1 N sulphuric acid resulted in some loss of nitrite and nitrate ion, possibly by reaction of nitrous acid with ethanol.) The aqueous ethanol solution was concentrated to a small volume on a rotary evaporator and the last trace of benzyl nitrate was extracted with petroleum ether. Nitrite and nitrate ion were separately reduced, following the procedure described in the previous section, and the ammonia absorbed in 0.01 N sulphuric acid. The extent of reaction was calculated from the total yield of ammonia obtained in the reductions. The solution of ammonium sulphate obtained from the reduction of nitrite ion was concentrated to about 3 ml and transferred to a high-vacuum system where it was oxidized by means of sodium hypobromite solution (18) to nitrogen gas for mass spectrometric analysis. The nitrogen was purified by continuous circulation over copper and copper oxide, both at 750° C, and through a trap cooled in liquid nitrogen.9 Sufficient ammonium sulphate was present to give on oxidation 2 ml of nitrogen at atmospheric pressure.

⁹Details of the purification procedure will appear in a subsequent publication.

CANADIAN JOURNAL OF CHEMISTRY, VOL. 38, 1960

Since the amount of nitrogen which would be formed from the nitrate ion produced in a single experiment would be much too small for mass spectrometric analysis, the ammonium sulphate solutions from all the nitrate ion reductions were combined and oxidized to give a single nitrogen sample for analysis.

The nitrogen isotopic abundance in the starting benzyl nitrate was determined as follows. Benzyl nitrate (0.04-0.05 M) was completely hydrolyzed by sodium ethoxide (0.05-0.10 M) in anhydrous ethanol at 60° C. An aliquot of 5 ml was then removed and the nitrite and nitrate reduced to ammonia by the method described in the section on Kinetic Measurements, except that no titration of ethoxide was performed and the ammonia from nitrite and nitrate was collected in the same acid solution. The ammonium sulphate solution was oxidized to nitrogen and the latter was measured mass spectrometrically as described previously. From two separate reactions carried out to completion a total of five nitrogen samples was prepared.

The mass spectrometric analysis was carried out using a 90° sector type instrument. similar to the one described by Wanless and Thode (29). It was capable of measuring relative isotopic abundance ratios, $N^{14} - N^{14}/N^{14} - N^{15}$, to $\pm 0.02\%$.

The kinetic isotope effect was calculated from the expression (19)

$$k_{14}/k_{15} = \frac{\ln(1-f)}{\ln(1-rf)}$$

...

$$r = \frac{(N^{14}/N^{15})_{\text{reactant}}}{(N^{14}/N^{15})_{NO2}}$$

and f = 0.09, the mole fraction of reactant which has undergone decomposition to nitrite ion.10

REFERENCES

1. R. BOSCHAN, R. T. MERROW, and R. W. VAN DOLAH. Chem. Revs. 55, 485 (1955). 2. J. W. BAKER and D. M. EASTY. I. Chem. Soc. 1193 (1952)

J. W. BAKER and D. M. EASTY. J. Chem. Soc. 1193, 1208 (1952).
 G. W. H. CHEESEMAN. J. Chem. Soc. 115 (1957).

- G. W. M. CHEESSMAN. J. CHEIL, SOC. 113 (1997).
 M. ANBAR, I. DOSTROVSKY, D. SAMUEL, and A. D. YOFFE. J. Chem. Soc. 3603 (1954).
 S. J. CRISTOL, B. FRANZUS, and A. SHADAN. J. Am. Chem. Soc. 77, 2512 (1955).
 W. D. EMMONS and J. P. FREEMAN. J. Am. Chem. Soc. 77, 4387, 4391 (1955).
 H. FEUER and C. SAVIDES. J. Am. Chem. Soc. 81, 5826 (1959).
 J. W. BAKER and T. G. HEGGS. J. Chem. Soc. 616 (1955).
 C. K. INGOLD. Structure and mechanism in organic chemistry. Cornell University Press, Ithaca, N.Y. 1953. Chap. VIII.
 S. J. CRISTOL and D. D. FIX. J. Am. Chem. Soc. 79, 3438 (1957).
 - 10. S.

- S. J. CRISTOL and D. D. FIX. J. Am. Chem. Soc. 75, 2647 (1953).
 S. J. CRISTOL and E. F. HOEGGER. J. Am. Chem. Soc. 79, 3438 (1957).
 H. H. JAFFÉ. Chem. Revs. 53, 191 (1953).
 S. J. CRISTOL and R. P. ARGANBRIGHT. J. Am. Chem. Soc. 79, 3441 (1957).
 P. S. SKELL and C. R. HAUSER. J. Am. Chem. Soc. 67, 1661 (1945).
 N. R. JONES and M. A. MACKENZIE. Talanta, 3, 356 (1960).
 K. B. WIBERG. Chem. Revs. 55, 713 (1955).
 J. E. VARNER, W. A. BULEN, S. VANECKO, and R. C. BURRELL. Anal. Chem. 25, 1528 (1953).
 D. RITTENBERG. In Preparation and measurement of isotopic tracers. J. W. Edwards. Ann Arbor, Michigane 1946 p. 31 D. RITTENBERG. In Preparation and measurement of isotopic tracers. J. W. F. Michigan. 1946. p. 31.
 W. H. STEVENS and R. W. ATTREE. Can. J. Research, B, 27, 807 (1949).
 C. H. DEPUY and C. A. BISHOP. J. Am. Chem. Soc. 82, 2532 (1960).
 J. BIGELEISEN. J. Chem. Phys. 17, 675 (1949).
 J. F. BROWN. J. Am. Chem. Soc. 77, 6341 (1955).
 J. BIGELEISEN and M. WOLFSBERG. Advances in Chem. Phys. 1, 15 (1958).
 G. AYREY. Private communication.

- W. H. SAUNDERS and D. H. EDISON. J. Am. Chem. Soc. 82, 138 (1960).
 W. H. SAUNDERS and D. H. EDISON. J. Am. Chem. Soc. 82, 138 (1960).
 A. F. FERRIS, K. W. MCLEAN, I. G. MARKS, and W. D. EMMONS. J. Am. Chem. Soc. 75, 4078 (1953).
 A. I. VOGEL. Practical organic chemistry. 3rd ed. Longmans, Toronto. 1956. p. 261.
 A. I. VOGEL. Practical organic chemistry. 3rd ed. Longmans, Toronto. 1956. p. 193.
 R. K. WANLESS and H. G. THODE. J. Sci. Instr. 30, 395 (1953).

¹⁰The error introduced by neglecting in the calculation of the isotope effect the 0.01 mole fraction of reactant which has produced nitrate ion without isotopic fractionation is insignificantly small.

2466

where