

SESSION V

II. INVESTIGATIONS OF ISOTOPE EFFECTS IN ORGANIC SYSTEMS (Part B)

Tritium and Deuterium Arrhenius Parameter Effects in a Base-promoted Elimination Reaction: Evidence for Tunnelling—
V. J. SHINER, JR. and B. MARTIN, *Indiana University, U.S.A.*

Question: The Bell treatment of tunnelling and the Johnston-Rapp treatment both lead to the conclusion that, in the presence of tunnelling, $k_H/k_D/k_T$ should be abnormal. Is your rate ratio D/T abnormal with respect to H/D? M. WOLFSBERG, *Brookhaven National Laboratory, U.S.A.*

Answer: The ratio of $(\log k_H/k_T)/(\log k_H/k_D)$ is 1.475 at 25° and 1.49 at 45°. These figures are significantly larger than the predicted value of 1.44 if the isotope effects are due only to loss of zero-point energy in one of the high-frequency modes, and I believe the deviations are in the direction predicted by tunnelling. SHINER

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Question: Do you have any evidence for curvature in plots either of $\ln(k_H)$ or of $\ln(k_H/k_D)$ versus $1/T$? M. WOLFSBERG, *Brookhaven National Laboratory, U.S.A.*

Answer: No. SHINER

Carbon-14 and Tritium Isotope Effects in Hofmann degradation of Quaternary Amines—H. SIMON and G. MÜLLHOFER, *Technische Hochschule Munchen, Germany*

Comment: The value obtained by Dr Smith and myself† has apparently caused you some difficulty. This result was part of a tracer experiment which was not done with the care usually exercised in isotope effect experiments. We accordingly set rather wide limits of experimental error on the number quoted. The largest source of error was uncertainty in temperature. In addition, our isotope effect was a combination of one primary and two secondary effects, which would be larger than the primary effect alone. V. J. SHINER, JR., *Indiana University, U.S.A.*

Reply: Dr Müllhofer and I looked for the k_H/k_T of $(\text{CH}_3)_3\text{N}^+\text{CH}_2\text{CH}_2\text{TOH}^-$, since we had a rather small value for the propyl base and a high value

† Reference 4.

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for the *p*-nitrophenethyl base, and a high value for the ethyl compound therefore seemed unlikely. We realize, of course, that your work was, in this case, not primarily intended to determine an accurate isotope effect. But Ayrey *et al.*† used your value as a cornerstone in support of their arguments. SIMON

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Comment: With regard to the question of the direction of asymmetry in the asymmetric transition state, the usual argument, based on the Hammond postulate, would place the proton nearest the weakest base in the transition state, which is, I believe, opposite to where you place it. I also believe that the results could be consistently interpreted in this alternative way. I would add, however, that the complex nature of the alkyl "base" may make the Hammond postulate difficult to apply in this case. V. J. SHINER, JR., *Indiana State University, U.S.A.*

Reply: I agree that the tritium isotope effects could be explained in the opposite way, but in view of the corresponding carbon-14 values our explanation seems more likely. SIMON

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Question: Do you bring all your isotope effects to one temperature by just assuming that the isotope effect is of the form $\exp(B/T)$? If so, is this not a somewhat dangerous procedure, since the correct expression might be $A \exp(B/T)$ with A different from unity? An instance of this is to be found in the paper presented by Dr Shiner§. M. WOLFSBERG, *Brookhaven National Laboratory, U.S.A.*

Answer: We assumed that the isotope effect is of the form $\exp(B/T)$. We did not measure temperature dependence, but our procedure should be good enough for the purpose of comparison. We measured, for example, the k_H/k_T for $(\text{CH}_3)_3\text{N}^+\text{—CH}_2\text{CH}_2\text{TOH}^-$ at 60° and 130°. We first estimated a value of 2.9 for 60°; then, on calculating a value on the basis of that measured at 130°, we again obtained a value of 2.9 for 60°. It does not necessarily follow, of course, that this good agreement will always be found. SIMON

Rate of Tritium Exchange in Diethyl methyl- d_3 -malonate-*t* and Diethyl malonate-*d,t* in Buffered Aqueous Solutions—D. E. SUNKO *et al.*, *Institute "Ruder Bošković," Yugoslavia*

Comment: With regard to the different isotope effects for deuteration of one or two γ -positions in the solvolysis of the cyclopentyl carbinyl derivative, it should be pointed out that the separate isotope effects, which might be thought to be the cause of this, would have to be quite large. Murr,

†Reference 5.

§These proceedings, *Pure Appl. Chem.* **8**, 731 (1964).

Heinemann and I have shown that the isotope effect caused by deuteration of only one of two positions which are equivalent in the initial state, but different in the transition state, would be expressed as $k_N/k_D = (2\alpha\alpha'/\alpha + \alpha')$ where α and α' are the k_N/k_D isotope effects in each of the two possible transition-state positions. Thus the separate isotope effects would have to be of the order of 40 per cent to explain the reported effect on the rate of deuteration of one of the ring gamma carbon atoms. V. J. SHINER, JR., *Indiana University, U.S.A.*

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Question: Are Dr Sunko's rather surprising results due to trace amounts of tritium in the D_2O used in the experiments? The methods used in the production of heavy water may cause a variable tritium enrichment. D. SAMUEL, *Weizmann Institute of Science, Israel*

Answer: I doubt it. If it were so it would have shown up in the experiment with diethyl-methyl-malonate-t in H_2O and D_2O respectively. In all cases D_2O from the same source was used. SUNKO

Titium and Nitrogen-15 Isotope Effects in the Decomposition of *p*-Nitrophenyltrimethylammonium iodide—E. M. HODNETT and J. J. SPARAPANY, *Oklahoma State University, U.S.A.*

Question: In contrast to Dr Hodnett we determined the intramolecular isotope effect k_H/k_T of *p*-nitrophenethyltrimethylammonium hydroxide directly. We degraded the compound at 22° in methanol-methoxide plus a trace of water. To this solution was added n-hexane and, by vigorous stirring, the *p*-nitrostyrene was dissolved in the hexane and little if any polymerization occurred. The styrene was brominated. You got your intramolecular isotope effect by calculation from the kinetic and the secondary isotope effects. Why do you have relatively wide deviations in your kinetic isotope effect measurements? What is the reason for the difference between your present values and those you published a few years ago? H. SIMON, *Technische Hochschule, Munich, Germany*

Answer: The value of 7.4 ± 2.8 for the intramolecular isotope effect which Dr Flynn and I reported earlier for this reaction† was extremely doubtful. The values for the intramolecular isotope effect which are reported in the present paper are much less doubtful, and we think that they are better than the one previously reported. However, these values are obtained by subtraction of two numbers of similar magnitude, both of which contain experimental error. Direct determination of the intramolecular isotope effect by the method you used has considerable merit.

Deviations in the value of kinetic isotope effects can occur in measuring the extent of reaction and the extent of molar radioactivity. Small amounts of impurities could affect both. We used a different synthesis

† Reference 2.

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for our starting compound (*p*-nitrophenethyltrimethylammonium iodide); this may have had some effect on our results. HODNETT

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Question: Some work that Dr Asperger has been carrying out recently suggests to me that the reversal of your secondary isotope effect in the non-aqueous solvent may be due to a change-over from an *E2* to an *E1* CB mechanism, particularly since your substrate would seem to make this more likely. Is there any evidence to support this suggestion? E. A. HALEVI, *Institute of Technology, Israel*

Answer: We have investigated the question of the *E1* CB mechanism for this reaction in aqueous solution and found no evidence for hydrogen exchange. However, we have not investigated hydrogen exchange in the alcoholic solution and have no direct evidence for or against the *E1* CB mechanism in this case. HODNETT