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Evidence of π-Complex Formation from the Solvent Isotope Effect on the Rate of Hydration of Olefins[1]

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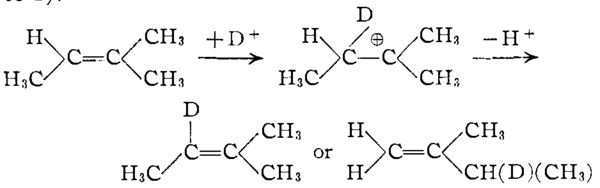
The effect of deuterium in the solvent on the aqueous acid-catalyzed rates of hydration of 2-methyl-2-butene and 1-methyl-1-cyclopentene has been determined. The results provide evidence that a facile proton transfer from hydronium ion to olefin precedes the rate-determining step. Since it has been shown that the conjugate acid formed cannot be a carbonium ion, the existence of a π-complex is implied.

Ciapetta and Kilpatrick using the chloroacetic acids made a determined effort to detect general acid catalysis in the hydration of isobutylene by aqueous acids.[3] Only specific hydronium ion catalysis was found. This result suggests, though it does not require, that the hydration mechanism involves a reversible proton transfer from hydronium ion to isobutylene preceding the rate-determining step.

On the other hand, Levy, Taft and Hammett have shown that olefin removed after 50% of the original has reacted contains no isomer in the hydration of either 2-methyl-2-butene or 2-methyl-1-butene.[4] This result excludes a reaction sequence in which carbonium ion is formed in a preliminary proton transfer, since these two olefins lead to the same carbonium ion (with all α-hydrogen atoms equivalent), which equilibrates at 25° to give 89% 2-methyl-2-butene and 11% 2-methyl-1-butene.[5]

We have obtained the equivalent result by carrying out the hydration of 2-methyl-2-butene by one molar nitric acid in 50% deuterated water. If a carbonium ion were formed preceding the rate-determining step it could be detected readily by the appearance of deuterium in the unreacted olefin during the course of the hydration reaction. The elimination of proton is substantially favored over that of the deuteron in the reverse step, both statistically (7 to 1) and kinetically (approximately 2 to 1).[6]



The olefin removed after one-half time of the reaction does not contain a detectable amount of deuterium. In Fig. 1, (A) is the infrared spectrum of a sample of pure 2-methyl-2-butene, (B) is that for a sample removed after the first half-life of a hydration experiment in 50% deuterated water; (C) is that for a sample of deuterated 2-methyl-2-butene.[7]

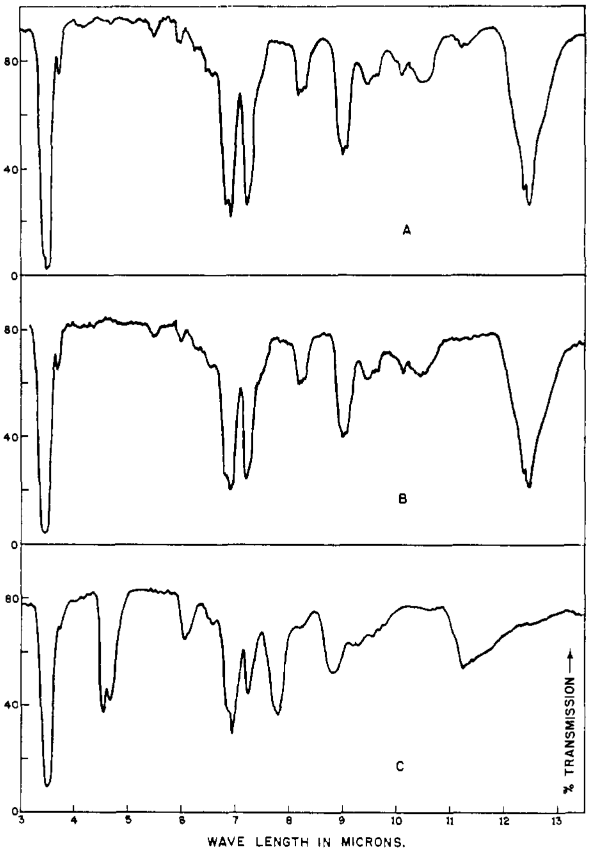


Fig. 1.—Infrared spectra: (A) pure 2-methyl-2-butene; (B) olefin sample removed after the first half-life of the hydration of 2-methyl-2-butene in 50% deuterated water; (C) sample of deuterated 2-methyl-2-butene.

One is clearly faced with only two alternatives: either the reaction involves a rate-determining proton transfer with a large Brönsted α (so that the only detectable catalyst is hydronium ion), or there is a preliminary proton transfer to give a conjugate acid of the olefin which loses in the reverse step the

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[1] The work reported herein was carried out on Project NR055-295 between the office of Naval Research and The Pennsylvania State University. Reproduction in whole or in part permitted for any purpose of the United States Government.

[2] Allied Chemical and Dye Corp. Fellow for 1953–1954; taken in part from the Ph.D. Thesis of E. Lee Purlee, The Pennsylvania State University, June, 1954.

[3] F. G. Ciapetta and M. Kilpatrick, THIS JOURNAL, **70**, 639 (1948).

[4] J. B. Levy, R. W. Taft, Jr., and L. P. Hammett, THIS JOURNAL, **75**, 1253 (1953).

[5] F. D. Rossini, K. S. Pitzer, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons," Carnegie Press, 1953, p. 475.

[6] J. V. Shiner, THIS JOURNAL, **75**, 2927 (1953); *cf.* also ref. 13.

[7] Prepared by shaking the olefin with acidified D_2O for an extended period under conditions such that the hydration reaction is appreciably reversible (about 50°); *cf.* ref. 13.

same proton added, *i.e.*, not all of the α-hydrogen atoms are equivalent in this conjugate acid.

In order to distinguish between these two alternatives we have determined the effect of D_2O content of the solvent on the rate of hydration of two olefins, 2-methyl-2-butene and 1-methyl-1-cyclopentene. According to generally accepted theory of the isotope effect, a rate-determining proton transfer is retarded by replacing H_3O^+ by D_3O^+.[8] An example is provided by the mutarotation of glucose for which the hydrogen-ion catalytic constant is 30% less in D_2O than H_2O.[9] On the other hand, the process involving the proton transfer preceding the rate-determining step is generally facilitated by 200 to 300% in D_2O relative to H_2O. This factor is attributed primarily to the greater acid strength of D_3O^+.

Bell,[8] following Gross,[10c] has suggested that a safer criterion for distinguishing between these two mechanisms is the following: The rate-determining proton transfer process should be retarded linearly with the mole fraction of deuterium, *n*, in the solvent, as Hamill and LaMer have observed for the mutarotation of glucose.[9] The solvent isotope effect (either facilitating or retarding) for the preliminary proton transfer mechanism should follow a relationship (non-linear in *n*) derived by Butler and his students based essentially upon the relative acidities of H_3O^+ and D_3O^+.[10] That is, according to this approach, a rate greater in D_2O than in H_2O is not the necessary criterion of a preliminary proton transfer, but instead it is the correlation of the solvent isotope effect by Butler's equation.

We have applied both criteria in an attempt to elucidate the olefin hydration mechanism.

Results

The rates of hydration at unit pressure of gaseous 2-methyl-2-butene by 0.973 *M* nitric acid of varying D_2O–H_2O content content were measured at 30.00°. The results are given in Table I. The experimental procedure used has been previously described.[11]

TABLE I

RATE CONSTANTS, k_p, FOR THE HYDRATION OF GASEOUS 2-METHYL-2-BUTENE BY 0.973 *M* NITRIC ACID SOLUTIONS OF VARYING D_2O–H_2O CONTENT AT 30.00° IN UNITS OF 10^4 MOLES-L.$^{-1}$-MIN.$^{-1}$

n[a]	k_p	$p.e.$[b]	k_n/k_H
0.000	2.58	0.03	(1.00)
.252	2.50	.01	0.97
.506	2.60	.03	1.01
.589	2.61	.025	1.01
.843	2.44	.01	0.95
.957	2.23	.01	0.86
1.000	2.12 (extrap.)		(0.82)

[a] $n = \Sigma(D)/\Sigma(H + D)$. [b] $p.e.$ = probable error of k_p, based upon the reproducibility of two to four experiments.

The rates of hydration at unit pressure of gaseous 1-methyl-1-cyclopentene by 0.0909 *M* nitric acid of varying D_2O–H_2O content at 35.20° have been obtained from measurements on the rate of the reversible dehydration of 1-methyl-1-cyclopentanol. The general experimental procedure and equations have been described earlier.[12] The modification in procedure necessary to prevent the results from being affected by deuteration of the carbinol is described in a subsequent paper.[13] The results are given in Table II.

TABLE II

RATE CONSTANTS, k_p, FOR THE HYDRATION OF GASEOUS 1-METHYL-1-CYCLOPENTENE BY 0.0909 *M* NITRIC ACID OF VARYING D_2O–H_2O CONTENT AT 35.20° IN UNITS OF 10^5 MOLES-L.$^{-1}$-MIN.$^{-1}$

n	k_p	$p.e.$	k_n/k_H
0.000	11.76	0.22	
.299	11.69	.22	0.99
.423	12.29	.20	1.05
.514	12.76	.46	1.08
.650	12.98	.44	1.10
.748	13.60	.58	1.16
.872	13.50	.50	1.15
.903	13.40	.59	1.14
.937	13.01	.42	1.11
1.000	12.7 (extrap.)		(1.08)

Butler's Equation.—This relationship has been derived on the basis of the following assumptions: (1) There is a proton transfer from solvent to substrate, S, preceding the rate-determining step

$$S + H^+ \underset{K}{\overset{\text{fast}}{\rightleftharpoons}} SH^+$$

$$SH^+ \underset{r}{\overset{\text{r.d.}}{\rightleftharpoons}} \text{products}$$

(2) The activity coefficient ratio, $f_{H^+} \cdot f_S/f_*$, is the independent of the H_2O–D_2O composition (f_* is the activity coefficient for the reaction transition state); (3) The ratio of the specific rate constants, r_D/r_H, for the rate-determining reaction of the deutero conjugate acid of the substrate to that for proto conjugate acid is independent of the H_2O–D_2O composition.

From the Brönsted rate equation one obtains the expressions:

In H_2O

$$k_H = \frac{-\mathrm{d}\ln(S)}{\mathrm{d}t} = r_H K_H (a_{H^+})_H \frac{f_S}{f_\pm} \qquad (1)$$

$(a_{H^+})_H$ = act. of the proton in ordinary water defined as $a_{H_3O^+}/a_{H_2O}$

K_H = thermodynamic equil. constant for the proton transfer step

r_H = rate constant for rate-determining reacn. of protonated substrate

In D_2O

$$k_D = \frac{-\mathrm{d}\ln(S)}{\mathrm{d}t} = r_D K_D (a_{D^+})_D \frac{f_s}{f_\pm} \qquad (2)$$

$(a_{D^+})_D$ = act. of the deuteron in heavy water defined as a_{D_3O}/a_{D_2O}

K_D = thermodynamic equil. constant for the deuteron transfer step

r_D = rate constant for rate-determining reacn. of deuterated substrate

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(8) (a) R. P. Bell, "Acid–Base Catalysis," Oxford Press, New York, N. Y., 1941, p. 150; (b) K. B. Wiberg, *Chem. Revs.*, **55**, 713 (1955).

(9) W. H. Hamill and V. K. LaMer, *J. Chem. Phys.*, **4**, 395 (1936).

(10) (a) W. J. C. Orr and J. A. V. Butler, *J. Chem. Soc.*, 330 (1937); (b) W. E. Nelson and J. A. V. Butler, *ibid.*, 958 (1938); (c) *cf.* also P. Gross, H. Steiner and H. Suess, *Trans. Faraday Soc.*, **32**, 883 (1936).

(11) J. B. Levy, R. W. Taft, Jr., D. Aaron and L. P. Hammett, THIS JOURNAL, **73**, 3792 (1952); E. L. Purlee, R. W. Taft, Jr., and C. A. DeFazio, *ibid.*, **77**, 837 (1955).

(12) R. W. Taft, Jr., J. B. Levy, D. Aaron and L. P. Hammett, *ibid.*, **74**, 4735 (1952).

(13) R. W. Taft, Jr., and E. L. Purlee, in preparation.

for a given acid concentration assumption 2 leads to

$$\frac{k_D}{k_H} = \frac{(r_D)}{r_H}\frac{(K_D)}{K_H} \tag{3}$$

For H_2O–D_2O mixtures

$$k_n = r_H K_H (a_{H^+})_n f_S/f_* + r_D K_D (a_{D^+})_n f_S/f_* \tag{4}$$

n = mole fraction of deuterium in the solvent $\Sigma D/\Sigma H + D$ and thus assumptions 2 and 3 give, dividing eq. 4 by 1, for a given acid concentration

$$\frac{k_n}{k_H} = \frac{(a_{H^+})_n}{(a_{H^+})_H} + k_D/k_H \frac{(a_{D^+})_n}{(a_{D^+})_D} \tag{5}$$

From the experimental k_D/k_H ratio and the functions $(a_{H^+})_n/(a_{H^+})_H$ and $(a_{D^+})_n/(a_{D^+})_D$, which Nelson and Butler have obtained from experimental and theoretical values for the equilibria between the isotopic species in acidified D_2O–H_2O mixtures, the k_n/k_H ratio can be calculated as a function of n.[10b]

Applied to the rate of hydration of olefins at unit pressure, S becomes olefin, and assumption 2 reduces to $f_{H^+}/f_* =$ constant. In making the calculations we have used the functions tabulated by Nelson and Butler. We note, however, that Nelson and Butler use the value 3.27 for the equilibrium constant for the reaction $H_2O + D_2O = 2\ HOD$. Urey has recently found this value to be incorrect, and instead the value 3.96 (very near the statistical value of 4.00) should be used.[14] The calculations of k_n/k_H values are only slightly sensitive to the value of this equilibrium constant provided that the same values for the other constants given by Nelson and Butler are used. We are presently re-examining the treatment of, and the data pertinent to, the Butler equation.

Discussion

Figure 2 shows a plot of the hydration rates, k_n/k_H, as a function of n, the mole fraction of deuterium in the solvent. The radius of each circle gives the probable error of the 2-methyl-2-butene points estimated from the results of two to four experiments under identical conditions. The dark vertical lines give the probable errors of the 1-methyl-1-cyclopentene points obtained in the same manner. The 2-methyl-2-butene data are more precise, having been obtained by direct measurement.

The full line in Fig. 2 gives the relationship between rate and n predicted by the Butler equation for a k_D/k_H ratio of 0.82. This is the value obtained from the trimethylethylene data by extrapolation to $n = 1.00$. The dashed line in Fig. 2 is that predicted for the k_D/k_H ratio of 1.08 obtained for 1-methyl-1-cyclopentene. It is apparent that the hydration rates of both olefins follow the Butler equation within the precision of these measurements.

The acid-catalyzed rates of decomposition of a diazoacetic ester, the inversion of sucrose, the bromination of acetone, the hydrolysis of acetal, ethyl orthoformate, ethyl formate, methyl acetate and some epoxides have been reported to follow the Butler equation with reasonable accuracy.[8,15] The unique forms which this relationship may assume (*cf.* Fig. 2, for example) and the fact that the relationship has been derived on the basis of a proton transfer preceding the rate-determining step, imply that reactions which involve a rate-determining proton transfer will not follow this equation. This conclusion is supported by the fact that the rates of mutarotation of glucose are linear with respect to n, and deviate widely from the Butler equation as illustrated in Table III.

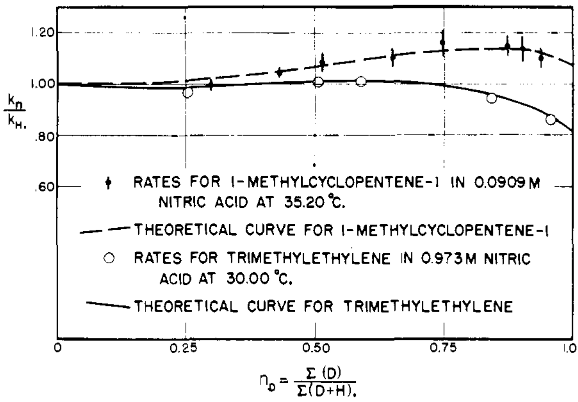

Fig. 2.—Hydration rates of trimethylethylene and 1-methylcyclopentene-1 as functions of H_2O–D_2O content of the solvent.

TABLE III

ISOTOPE EFFECT ON THE MUTAROTATION OF GLUCOSE. FAILURE OF BUTLER'S EQUATION TO APPLY

n	(k_n/k_H) Obsd.[a]	Calcd. eq. 5
0.20	0.95	0.99
.40	.89	.99
.60	.84	.99
.80	.78	.93
1.00	.72	(.72)

[a] Interpolated values.

Thus our results in H_2O–D_2O mixtures provide evidence according to the present mechanistic theory of the solvent isotope effect that there exists a preliminary reversible proton transfer from hydronium ion to olefin. Since the resulting conjugate-acid of the olefin cannot be a carbonium ion, the only reasonable structure suggested by bond theory is that of a π-complex. Its structure is pictured as planar about the C=C double bond with a proton embedded in the π-orbital perpendicular to this plane.[16] The π-proton is clearly not equivalent to those originally bonded (by sp^2 or sp^3 orbitals) in the olefin. All of the data on the olefin hydration reaction appear to be uniquely consistent with the π-complex as the conjugate-acid produced from olefin in the reversible proton transfer step, provided that only the proton bonded to the π-orbital exchanges rapidly with the acidic media. Solubility data indicate that the π-complex is a high energy intermediate as are the conjugate-acid intermediates in other reactions which follow the Butler equation.[17]

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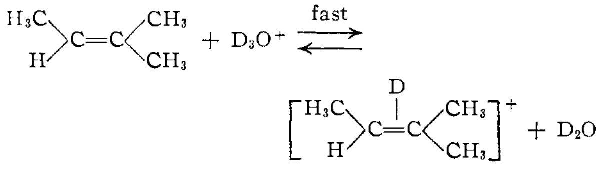
(14) H. C. Urey, *J. Chem. Soc.*, 569 (1947).

(15) J. G. Pritchard and F. A. Long, THIS JOURNAL, **78**, Dec. (1956).

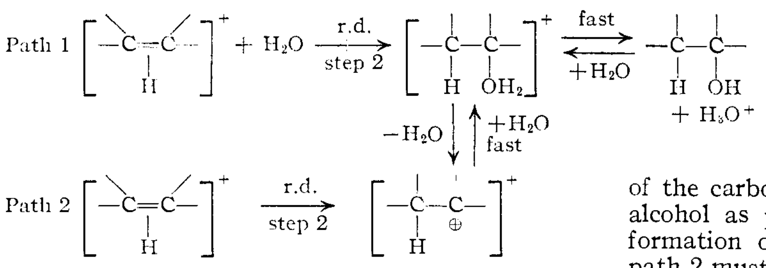
(16) M. J. S. Dewar, *J. Chem. Soc.*, 406 (1946); C. C. Price, "Mechanisms of Reactions at the Carbon–Carbon Double Bond," Interscience Publishers, Inc., New York, N. Y., 1946, p. 46.

(17) E. L. Purlee and R. W. Taft, Jr., THIS JOURNAL, **78**, 5811 (1956).

Consequently, it appears that step 1 in the hydration reaction is best represented by the equation



The near unit isotope effect ($k_D/k_H \cong 1.0$) observed in the present reactions is the first case of its kind reported. The reactions listed above which follow Butler's equation have k_D/k_H ratios substantially greater than unity—generally from two to three. However, according to the accepted mechanisms for these reactions the added proton is not directly involved in the rate-determining step, and thus the r_D/r_H ratio of eq. 3 is probably near unity for these reactions.



In the olefin hydration reaction, however, the near unit isotope may be accounted for on the following basis. The rate-determining step (step 2) involves the transfer of the hydrogen from its position in the π-complex to an adjacent carbon atom to form a conventional C–H bond. The rate of this internal hydrogen migration is retarded by deuterium (a factor of about two has been observed for the isotope effect in hydrogen migration reactions[18]). Thus the observed k_D/k_H ratios of near unity may be attributed (eq. 3) to the resultant, $k_D/k_H = K_Dr_D/K_Hr_H$, of the two opposing factors, the preliminary equilibrium step which is favored by D ($K_D/K_H \cong 2.0$), and the rate-determining step which is retarded by D ($r_D/r_H \cong 0.5$). The fact that the k_D/k_H ratio is in one case slightly greater than unity and in the other slightly less is also reasonably accounted for on the basis of small differences in the effect of structure on the opposed factors.

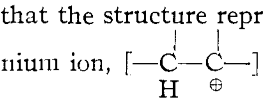
Alternately, we may make the equivalent conclusion that the observed isotope effect indicates that the proton is as strongly bound in the reaction transition state as in the ground state. According to the mechanistic theory of the isotope effect, this condition indicates that the proton is probably introduced in a step preceding the rate-determining one.

The latter argument appears to be somewhat more convincing if the conventional rate constants for dissolved olefin at unit concentration are used. We have determined the solubility of 2-methyl-2-butene in both light and heavy water at 30.00°. The value obtained in the former is $4.89 \pm 0.03 \times 10^{-3}$ mole-l.$^{-1}$-atm.$^{-1}$, and in the latter $4.40 \pm 0.03 \times 10^{-3}$ mole-l.$^{-1}$-atm.$^{-1}$. Assuming the same relative solubility in 0.973 M nitric acid, the k_D/k_H ratio for rates at unit concentration of dissolved olefin is 0.90. Inasmuch as k_D/k_H values of slightly less than unity are observed for both the hydration of 2-methyl-2-butene and previously investigated reactions which are thought to involve a rate-determining proton transfer from hydronium ion,[8b] there is a certain probability that the olefin hydration is also of this kind. The fact that k_D/k_H for 1-methyl-1-cyclopentanol is greater than unity as well as the other results discussed above argue for a low probability of such a mechanism.

The present results do not appear to distinguish between the following reasonable paths for the rate-determining and subsequent steps of the overall reaction given here.

Evidence favoring path 2 has been presented.[19]

The recent results of Dostrovsky and Klein are of interest in this connection.[20] The acid-catalyzed O^{18} exchange between *t*-butyl alcohol and water has been found to be about twenty-fold greater than the rate of formation of isobutylene. If the mechanism of this exchange involves a rate-determining formation of the carbonium ion from the protonated *t*-butyl alcohol as proposed by these authors, then the formation of π-complex from *t*-butyl alcohol by path 2 must involve a subsequent rate determining step (*i.e.*, step 2), in accord with the evidence presented in Fig. 1.

It should be mentioned that the structure representing the solvated carbonium ion,  $[\underset{H}{\overset{|}{—C}}—\underset{\oplus}{\overset{|}{C}}—]^+$, is not well defined. It is not presently known, for example, whether the interactions between the positive carbon and water molecules of the solvent are sufficient to preserve the stereochemical integrity so that the hydration–dehydration process is stereospecific as Hammond and Nevitt have observed for the hydrogen bromide addition to dimethylcyclohexenes in glacial acetic acid.[21]

The olefin hydration reaction and the decomposition of diazoacetic ester make an interesting study in contrast. Both reactions exhibit specific hydronium ion catalysis and both follow the Butler equation in H_2O–D_2O mixtures (for the latter, $k_D/k_H = 2.13$[8]). In contrast to our present findings, Roberts, *et al.*,[22] have obtained convincing evidence of the formation of a conjugate acid of diazoacetic ester with both α-H atoms equivalent: $[N_2—CH_2—CO_2C_2H_5]^+$.

Acknowledgment.—We are pleased to acknowledge the suggestion of Professor J. D. Roberts which led to the present study.

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[18] *Cf.* P. D. Bartlett and J. D. McCollum, This Journal, **78**, 1448 (1956).

[19] R. W. Taft, Jr., E. L. Purlee, P. Riesz and C. A. DeFazio, This Journal, **77**, 1584 (1955); P. Riesz, R. H. Boyd and R. W. Taft, Jr., *ibid.*, in preparation.

[20] I. Dostrovsky and F. S. Klein, *J. Chem. Soc.*, 791 (1955).

[21] G. S. Hammond and T. D. Nevitt, This Journal, **76**, 4121 (1954).

[22] J. D. Roberts, C. M. Regan and I. Allen, *ibid.*, **74**, 3679 (1952).

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