

## Thermal Isomerization of Isopropyl1,1,1d 3 Radicals

W. M. Jackson and J. R. McNesby

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shown in Fig. 6. The quadrupole terms in this case do not contribute significantly, even for  $J=1$ .

Of course in any experiment on a heteronuclear molecule in the limit of frequent collisions, to which (10) and (11) apply, one is in practice dealing with a mixture of several rotational states. Under the assumption that changes in  $J$  are infrequent, however,<sup>9,10</sup> one can still hope to settle the question of collisional selection rules by measuring the temperature dependences

of the relaxation times. Measurements of this kind are now under way in this laboratory.

#### ACKNOWLEDGMENTS

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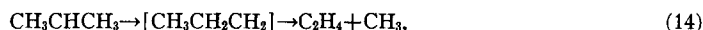
### Thermal Isomerization of Isopropyl-1,1,1-*d*<sub>3</sub> Radicals

W. M. JACKSON AND J. R. McNESBY

National Bureau of Standards, Washington, D. C.

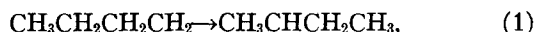
(Received November 10, 1961)

The unimolecular isomerization of isopropyl radicals was investigated by studying the thermal decomposition of pure  $\text{CD}_3\text{CH}_2\text{CH}_3$  from 472° to 553°C. Isomerization of  $\text{CD}_3\text{CHCH}_3$ , was detected by measuring  $\text{CD}_2\text{CHD}$  formed from the isomerized radical. The net result of isomerization is reaction (14).



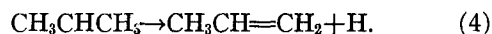
It is found that isomerization of isopropyl up to 500°C proceeds at a rate, relative to decomposition via reaction (15), which can be described by  $k_{14}/k_{15} \leq 0.07$ . A mechanism which produces methyl and ethylene directly without intermediate isomerization gives  $k_{14}/k_{15} \leq 0.04$  at 500°C. Contrary to other published estimates of  $k_{14}/k_{15}$ , the latter shows no downward trend with increasing temperature.

THE rate of the unimolecular homogeneous isomerization of alkyl radicals may be viewed as a process which is in competition with other reactions of the same radical. For instance, the isomerization of *n*-butyl radicals [reaction (1)] in order to be observed, must compete successfully with the simple decomposition of the radicals [reaction (2)].



It has been shown that up to 500°C, isomerization is not competitive with simple decomposition for *n*-butyl, isobutyl, and sec-butyl radicals<sup>1-4</sup> although the experiments of Kerr and Trotman-Dickenson<sup>5</sup> had been interpreted to favor isomerization of *n*-butyl radicals.

A more interesting case is isomerization of the isopropyl radical.



The *n*-propyl radical formed in reaction (3) has a very high probability for decomposition at temperatures where *i*-propyl decomposes as in reaction (4). It is possible that isopropyl decomposes directly to methyl and ethylene without the preliminary isomerization to *n*-propyl. In the discussion that follows, the term isomerization signifies the production of methyl and ethylene from the isopropyl radical whether or not *n*-propyl is, in fact, the intermediate.

Isomerization [reaction (3)] is much more likely to be competitive with the simple decomposition [reaction (4)] than in the *n*-butyl case [reactions (1) and (2)], since, on the basis of bond strength data,<sup>6</sup> the activation energy for the simple decomposition of *i*-propyl is about 10 kcal more than that for the decomposition of *n*-butyl, while  $E_3$  is probably only a few

<sup>1</sup> F. E. Frey and H. J. Hepp, J. Am. Chem. Soc. **55**, 3357 (1933).

<sup>2</sup> J. R. McNesby, C. M. Drew, and A. S. Gordon, J. Chem. Phys. **24**, 1260 (1956).

<sup>3</sup> F. P. Lossing and J. B. de Sousa, J. Am. Chem. Soc. **81**, 280 (1959).

<sup>4</sup> A. S. Gordon and J. R. McNesby, J. Chem. Phys. **33**, 1882 (1960).

<sup>5</sup> J. A. Kerr and A. F. Trotman-Dickenson, J. Chem. Soc. **1960**, 1602.

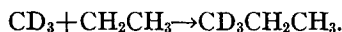
<sup>6</sup> T. L. Cottrell, *The Strengths of Chemical Bonds* (Butterworths Scientific Publication, London, 1958).

kcal in excess of  $E_1$ . It follows that for the isopropyl radical, isomerization has a higher probability of competing successfully with decomposition than in the case of *n*-butyl. Evidence obtained by Heller and Gordon<sup>7</sup> and by Kerr and Trotman-Dickenson<sup>8</sup> on the photolyses of diisopropyl ketone and isobutyraldehyde, respectively, indicates that isomerization may be from 10 to 50% as important as decomposition at 472°. The present work employs the thermal decomposition of propane-1,1,1-*d*<sub>3</sub> in which it is possible to observe the isomerization of *i*-propyl-1,1,1-*d*<sub>3</sub>.

## I. EXPERIMENTAL

### A. Isotopic Integrity of CD<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>

A standard sample of propane-1,1,1-*d*<sub>3</sub> was prepared by gas phase photolysis of mixtures of CD<sub>3</sub>COCD<sub>3</sub> (99.5 at. % D) and CH<sub>3</sub>CH<sub>2</sub>COCH<sub>2</sub>CH<sub>3</sub> using a medium pressure mercury arc. The elementary process responsible for the formation of propane is



The propane-1,1,1-*d*<sub>3</sub> was extracted from the resulting reaction mixture by gas chromatography using a 2-m silica gel column at 90°C. The propane-1,1,1-*d*<sub>3</sub> was then passed over ascarite and Drierite to remove CO<sub>2</sub> and water and was frozen and pumped to a high vacuum at 77°K. The mass spectrum of the propane-1,1,1-*d*<sub>3</sub> was then measured. After several unsuccessful attempts, Merck & Company, Montreal, produced propane-1,1,1-*d*<sub>3</sub> whose mass spectrum compared very well with our synthetic material. A chemical test for isotopic purity was next carried out both on our standard material and the Merck material. The method takes advantage of the fact that methyl radicals are produced from *n*-propyl radicals formed in the thermal decomposition of propane-1,1,1-*d*<sub>3</sub>.



If any CHD<sub>2</sub>CHDCH<sub>3</sub> is present in the deuterated propane, the pyrolysis will produce CHD<sub>2</sub> radicals, most of which will abstract H and appear as CH<sub>2</sub>D<sub>2</sub>. Thus the CH<sub>2</sub>D<sub>2</sub>/CD<sub>3</sub>H ratio is a measure of the relative amounts of CHD<sub>2</sub> and CD<sub>3</sub> groups in the deuterated propane. The first commercial preparations of deuterated propane were rejected on the basis that large CH<sub>2</sub>D<sub>2</sub>/CD<sub>3</sub>H ratios were observed in the pyrolysis and that their mass spectra indicated that CHD<sub>2</sub> groups were present. Pyrolysis of the final preparation from Merck and Company showed no detectable CH<sub>2</sub>D<sub>2</sub>, and an upper limit of about 0.02 was placed

upon the ratio of CHD<sub>2</sub>/CD<sub>3</sub> groups in the deuterated propane. The importance of establishing this upper limit will be evident for the critical measurement to be made is the abundance of CHD=CD<sub>2</sub> in the products of the propane-1,1,1-*d*<sub>3</sub> pyrolysis. It is very important to exclude the radical CD<sub>2</sub>CHDCH<sub>3</sub> formed from CHD<sub>2</sub>CHDCH<sub>3</sub> or CD<sub>3</sub>CHDCH<sub>3</sub> since its decomposition produces CHD=CD<sub>2</sub>. The species CD<sub>3</sub>CHDCH<sub>3</sub> is absent since the mass spectrum of the deuterated material showed less than 0.2% propane-*d*<sub>4</sub>. The species CH<sub>2</sub>DCD<sub>2</sub>CH<sub>3</sub> is absent since evidence for CH<sub>2</sub>D groups is negative.

### B. Chemical Purity of CD<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub>

Finally the CD<sub>3</sub>CH<sub>2</sub>CH<sub>3</sub> was purified by gas chromatography. A sample of the resulting material was passed again through the chromatograph and the effluent stream trapped where ethylene would appear. The contents of the trap were then analyzed by mass spectrometry and no detectable ethylene was found to be present.

### C. Procedure

The experimental system has been described elsewhere.<sup>9</sup> The reaction vessel was of quartz and about 50 cc in volume. Approximately 50 mm of propane-1,1,1-*d*<sub>3</sub> was admitted to the hot reaction vessel and immediately after reaction had taken place the reaction mixture was pumped into a sample flask for analysis. Metal bellows valves were used throughout and no grease or wax was used in any part of the reaction system or analytical system. The reaction mixture was injected into a gas chromatograph using a 2-m silica gel column at 90° and the ethylene fraction was trapped at 77°K. The peak areas of ethylene and propylene were measured and the ethylene/propylene ratio was determined by comparing the chromatographic record with those of known mixtures of ethylene and propylene. The ethylene trapped after elution from the chromatograph was analyzed in the mass spectrometer. Ethylene-*d*<sub>3</sub> was always small and contributed little to the parent peaks of CH<sub>2</sub>=CD<sub>2</sub> and CH<sub>2</sub>=CH<sub>2</sub>. The mass spectrum of pure CH<sub>2</sub>=CD<sub>2</sub> (purity verified by infrared analysis<sup>10</sup>) was measured on the mass spectrometer in order to permit analysis of the mixture. In this way the ratio,

$$\text{CHD}=\text{CD}_2 / (\text{CHD}=\text{CD}_2 + \text{CD}_2=\text{CH}_2 + \text{CH}_2=\text{CH}_2),$$

was measured. The reactions were carried out to about one percent decomposition of propane-1,1,1-*d*<sub>3</sub>.

## II. RESULTS AND DISCUSSION

The approach used in the present work was to produce thermal propyl radicals by abstraction of H and D

<sup>7</sup> C. A. Heller and A. S. Gordon, J. Phys. Chem. **62**, 709 (1958).

<sup>8</sup> J. A. Kerr and A. F. Trotman-Dickenson, Trans. Faraday Soc. **54**, 921 (1958).

<sup>9</sup> W. M. Jackson and J. R. McNesby, J. Am. Chem. Soc. **83**, 489 (1961).

<sup>10</sup> H. Okabe and J. R. McNesby, J. Chem. Phys. **36**, 601 (1962).

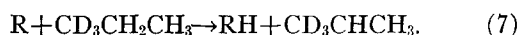
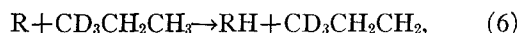
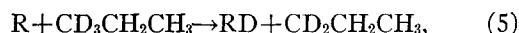
TABLE I. Isomerization of isopropyl radicals.

$T^{\circ}\text{C}$	$k_{14}/k_{15}$		$\alpha$	This work		Ref. 8		Ref. 7
	Total ethylene Total propylene	$\text{C}_2\text{HD}_3$ Total ethylene		Isom.	No. isom.	a	b	
472	0.8	0.027	0.37	0.077	0.042	0.089	0.23	0.54
503	0.9	0.023	0.38	0.072	0.040	0.073	0.18	0.50
529	(1.0)	0.031	0.39	0.11	0.062	0.062	0.14	0.48
553	1.0	0.027	0.40	0.092	0.053	0.055	0.12	0.45

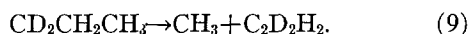
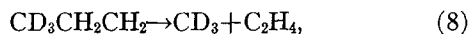
<sup>a</sup> Based on ethylene yield in *i*-butyraldehyde photolysis.

<sup>b</sup> Based on methane yield in *i*-butyraldehyde photolysis.  $\alpha$  is the kinetic deuterium isotope effect.

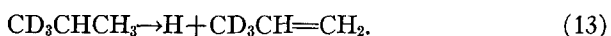
from  $\text{CH}_3\text{CH}_2\text{CD}_3$  by radicals generated in the thermal decomposition of  $\text{CD}_3\text{CH}_2\text{CH}_3$ .



Simple decomposition of the *n*-propyl radicals to methyl and ethylene has been shown by isotope techniques to be the only important thermal unimolecular reaction of *n*-propyl.<sup>9</sup>



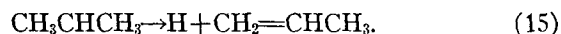
It is evident that no mechanism exists for the production of ethylene containing more than two D atoms from *n*-propyl. The isopropyl radical, however, should give  $\text{C}_2\text{D}_3\text{H}$  if isomerization is competitive with the simple decompositions (12) and (13).



It is well known that the decomposition of *n*-propyl proceeds very much faster than that of *i*-propyl so that in the temperature region where isopropyl decomposes efficiently as in (12) and (13), it is a good approximation that every *n*-propyl formed in reactions (10) and (11) is revealed as  $\text{CD}_2\text{CHD}$  and  $\text{C}_2\text{H}_4$ . Since  $\text{C}_2\text{H}_4$  is formed directly in reaction (8) as well as by reaction (11), isomerization can only be detected by measuring the  $\text{CD}_2\text{CHD}$  formed in reaction (10).

The ratio of the ethylene resulting from isomerization, to the propylene formed by decomposition of *i*-propyl, gives the ratio of the respective rate constants

corresponding to the ratio  $k_{14}/k_{15}$  reported by Heller and Gordon<sup>7</sup> and by Kerr and Trotman-Dickenson.<sup>8</sup>



The following assumptions are made:  $k_{11} = \frac{1}{2}k_{14}$ ;  $k_{10} = \frac{1}{2}\alpha k_{14}$ ;  $k_{13} = \frac{1}{2}k_{15}$ ;  $k_{12} = \frac{1}{2}\alpha k_{15}$ , where  $\alpha$  is a factor less than unity which reflects the isotope effect and is assumed to be of the same magnitude for isomerization and for H atom expulsion. It follows that

$$\frac{k_{10} + k_{11}}{k_{12} + k_{13}} = \frac{\frac{1}{2}k_{14}(1 + \alpha)}{\frac{1}{2}k_{15}(1 + \alpha)} = \frac{k_{14}}{k_{15}} = \frac{\text{C}_2\text{HD}_3(1 + 1/\alpha)}{\text{CD}_2=\text{CHCH}_3 + \text{CD}_3\text{CH}=\text{CH}_2}. \quad (1')$$

The experimental measurement of the right-hand side of Eq. (1') was made by first measuring total ethylene/total propylene by means of gas chromatography on a silica gel column. The ethylene fraction was trapped upon elution from the chromatographic column and the ratio  $\text{C}_2\text{HD}_3$ /total ethylene was measured on a mass spectrometer. From Eq. (1')

$$\frac{\text{total ethylene}}{\text{total propylene}} \frac{\text{C}_2\text{HD}_3(1 + 1/\alpha)}{\text{total ethylene}} = \frac{k_{14}}{k_{15}}. \quad (2')$$

Now, if reaction (14) proceeds directly to  $\text{CH}_3$  and  $\text{C}_2\text{H}_4$  it might be expected that no substantial isotope effect will be operative, i.e.,  $\alpha = 1$ . In this case we obtain  $(k_{14}/k_{15})_{\text{no. isom.}}$ . If, however, there is an isotope effect because of intermediate isomerization of isopropyl to *n*-propyl,  $\alpha$  will be less than unity. Since  $\alpha$  has not been measured, it is necessary to be somewhat arbitrary and we use here  $\alpha = \exp(-1500/RT)$ , the magnitude of the isotope effect for abstraction of H and D by methyl radicals.<sup>11</sup> The result so obtained gives  $(k_{14}/k_{15})_{\text{isom.}}$ . The results are summarized in Table I.

<sup>11</sup> J. R. McNesby, J. Am. Chem. Soc. **64**, 1671 (1960).

A possible mechanism not involving isomerization of isopropyl and one which should have no substantial deuterium isotope effect is



It is apparent that if isopropyl decomposes directly into  $\text{CH}_3$  and ethylene as suggested by Kerr and Trotman-Dickenson,<sup>8</sup> without isomerization, the value of  $k_{14}/k_{15}$  has an upper limit of about 0.05 from 472°–553°C with no evident trend. From 2–3% of the ethylene is  $\text{CHD}=\text{CD}_2$ , and it must be admitted that small amounts of  $\text{CHD}_2\text{CDHCH}_3$  in the original propane as well as  $\text{CD}_3\text{CDHCH}_3$  formed by abstraction of D by isopropyl could contribute to this figure. It is probably safe to conclude that there is no serious disagreement between the present results and those of Kerr and Trotman-Dickenson<sup>8</sup> obtained by measuring the ethy-

lene yield in isobutyraldehyde photolysis, except that our results show that isomerization does not increase in relative importance as the temperature is lowered. The results obtained by isobutyraldehyde photolysis<sup>8</sup> on the basis of the methane yield are, however, not in agreement with the present work. It is very difficult to explain the very high isomerization rate constants reported by Heller and Gordon<sup>7</sup> from their study of diisopropyl ketone-*d*<sub>2</sub> photolysis. Since most of the isopropyl radicals formed in the latter work were produced in the primary photochemical act, the possibility that they were vibrationally excited is suggested. A further possible source of uncertainty in this work is that all but one of the experiments were carried out to at least 6.5% conversion. Under these conditions, secondary reactions of H atoms with propylene to produce *n*-propyl radicals introduce a possible source of error.

## Magnetic Properties of Hydrogen Fluoride. I. Rotational Moment\*

T. P. DAS

*Department of Physics, University of California, Riverside, California*

AND

MARTIN KARPLUS†

*Department of Chemistry and Watson Scientific Computing Laboratory, Columbia University, New York, New York*

(Received November 6, 1961)

A variation-perturbation formulation is presented for the calculation of the electronic contribution to the rotational energy and magnetic moment of a  $\Sigma$  molecule. An application of the method to a one-center single-configuration wave function for hydrogen fluoride is given and compared with a two-center function result. The calculated magnetic moment is found to be 0.9276 nuclear magnetons for the one-center function and 0.6354 nuclear magnetons for the two-center function in comparison with the experimental value of 0.7392 nuclear magnetons. Analysis of the results shows that the nuclear charges make the dominant contribution and that the electronic "slippage" is almost complete. Furthermore, the convergence of the variational expansion indicates that a significant improvement in the theoretical value probably requires refinements in the ground-state wave function.

### I. INTRODUCTION

THE magnetic properties of molecules are an important source of information about their electronic structure.<sup>1,2</sup> Even in essentially nonmagnetic systems (e.g.,  $\Sigma$  molecules) the interactions with a magnetic field are of considerable interest. An external field or the molecular rotation induces a small magnetic moment whose magnitude and orientation is governed by the properties of the electron distribution. Since the

additional energy contributed to the molecule is generally minute compared to the internal electronic energy, the magnetic interaction can be treated effectively by the methods of perturbation theory. This makes feasible the calculation of susceptibilities and induced moments from ground-state wave functions valid in the absence of any external field. Comparisons of the resulting theoretical values with quantitative experimental data can be used to test approximate wave functions, as well as to aid in the interpretation of the magnetic measurements.

Although most of the previous calculations of magnetic properties have been limited to the hydrogen molecule,<sup>1</sup> recent experimental and theoretical developments suggest that detailed studies of more complex

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† Alfred P. Sloan Foundation Fellow.

<sup>1</sup> T. P. Das and R. Bersohn, *Phys. Rev.* **115**, 897 (1959).

<sup>2</sup> M. Karplus, *Revs. Modern Phys.* **32**, 458 (1960).