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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,[9,10] 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.

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Thermal Isomerization of Isopropyl-1,1,1-d_3 Radicals

W. M. JACKSON AND J. R. MCNESBY
National Bureau of Standards, Washington, D. C.

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The unimolecular isomerization of isopropyl radicals was investigated by studying the thermal decomposition of pure $CD_3CH_2CH_3$ from 472° to 553°C. Isomerization of CD_3CHCH_3, was detected by measuring CD_2CHD formed from the isomerized radical. The net result of isomerization is reaction (14).

$$CH_3CHCH_3 \rightarrow [CH_3CH_2CH_2] \rightarrow C_2H_4 + CH_3, \tag{14}$$

$$CH_3CHCH_3 \rightarrow CH_3CH{=}CH_2 + H. \tag{15}$$

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 $k_{14}/k_{15} \leqslant 0.07$. A mechanism which produces methyl and ethylene directly without intermediate isomerization gives $k_{14}/k_{15} \leqslant 0.04$ 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)].

$$CH_3CH_2CH_2CH_2 \rightarrow CH_3CHCH_2CH_3, \tag{1}$$

$$CH_3CH_2CH_2CH_2 \rightarrow CH_3CH_2 + CH_2{=}CH_2. \tag{2}$$

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

A more interesting case is isomerization of the isopropyl radical.

$$CH_3CHCH_3 \rightarrow CH_2CH_2CH_3, \tag{3}$$

$$CH_3CHCH_3 \rightarrow CH_3CH{=}CH_2 + H. \tag{4}$$

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,[6] 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

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[5] J. A. Kerr and A. F. Trotman-Dickenson, J. Chem. Soc. **1960**, 1602.

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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[7] and by Kerr and Trotman-Dickenson[8] 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_3 in which it is possible to observe the isomerization of *i*-propyl-1,1,1-d_3.

I. EXPERIMENTAL

A. Isotopic Integrity of $CD_3CH_2CH_3$

A standard sample of propane-1,1,1-d_3 was prepared by gas phase photolysis of mixtures of CD_3COCD_3 (99.5 at. % D) and $CH_3CH_2COCH_2CH_3$ using a medium pressure mercury arc. The elementary process responsible for the formation of propane is

$$CD_3+CH_2CH_3\rightarrow CD_3CH_2CH_3.$$

The propane-1,1,1-d_3 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_3 was then passed over ascarite and Drierite to remove CO_2 and water and was frozen and pumped to a high vacuum at 77°K. The mass spectrum of the propane-1,1,1-d_3 was then measured. After several unsuccessful attempts, Merck & Company, Montreal, produced propane-1,1,1-d_3 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_3.

$$CH_2CH_2CD_3\rightarrow CD_3+CH_2{=}CH_2,$$

$$CH_3CH_2CD_2\rightarrow CH_3+CH_2{=}CD_2.$$

If any CHD_2CHDCH_3 is present in the deuterated propane, the pyrolysis will produce CHD_2 radicals, most of which will abstract H and appear as CH_2D_2. Thus the CH_2D_2/CD_3H ratio is a measure of the relative amounts of CHD_2 and CD_3 groups in the deuterated propane. The first commercial preparations of deuterated propane were rejected on the basis that large CH_2D_2/CD_3H ratios were observed in the pyrolysis and that their mass spectra indicated that CHD_2 groups were present. Pyrolysis of the final preparation from Merck and Company showed no detectable CH_2D_2, and an upper limit of about 0.02 was placed upon the ratio of CHD_2/CD_3 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 $CHD{=}CD_2$ in the products of the propane-1,1,1-d_3 pyrolysis. It is very important to exclude the radical CD_2CHDCH_3 formed from CHD_2CHDCH_3 or CD_3CHDCH_3 since its decomposition produces $CHD{=}CD_2$. The species CD_3CHDCH_3 is absent since the mass spectrum of the deuterated material showed less than 0.2% propane-d_4. The species $CH_2DCD_2CH_3$ is absent since evidence for CH_2D groups is negative.

B. Chemical Purity of $CD_3CH_2CH_3$

Finally the $CD_3CH_2CH_3$ 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.[9] The reaction vessel was of quartz and about 50 cc in volume. Approximately 50 mm of propane-1,1,1-d_3 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_3 was always small and contributed little to the parent peaks of $CH_2{=}CD_2$ and $CH_2{=}CH_2$. The mass spectrum of pure $CH_2{=}CD_2$ (purity verified by infrared analysis[10]) was measured on the mass spectrometer in order to permit analysis of the mixture. In this way the ratio,

$$CHD{=}CD_2/(CHD{=}CD_2+CD_2{=}CH_2+CH_2{=}CH_2),$$

was measured. The reactions were carried out to about one percent decomposition of propane-1,1,1-d_3.

II. RESULTS AND DISCUSSION

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

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TABLE I. Isomerization of isopropyl radicals.

				k_{14}/k_{15}				
	Total ethylene	C_2HD_3		This work		Ref. 8		
T°C	Total propylene	Total ethylene	α	Isom.	No. isom.	a	b	Ref. 7
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

[a] Based on ethylene yield in i-butyraldehyde photolysis.

[b] Based on methane yield in i-butyraldehyde photolysis. α is the kinetic deuterium isotope effect.

from $CH_3CH_2CD_3$ by radicals generated in the thermal decomposition of $CD_3CH_2CH_3$.

$$R+CD_3CH_2CH_3 \rightarrow RD+CD_2CH_2CH_3, \quad (5)$$

$$R+CD_3CH_2CH_3 \rightarrow RH+CD_3CH_2CH_2, \quad (6)$$

$$R+CD_3CH_2CH_3 \rightarrow RH+CD_3CHCH_3. \quad (7)$$

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.[9]

$$CD_3CH_2CH_2 \rightarrow CD_3+C_2H_4, \quad (8)$$

$$CD_2CH_2CH_3 \rightarrow CH_3+C_2D_2H_2. \quad (9)$$

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 C_2D_3H if isomerization is competitive with the simple decompositions (12) and (13).

$$CD_3CHCH_3 \rightarrow [CD_2CHDCH_3] \rightarrow CD_2CHD+CH_3, \quad (10)$$

$$CD_3CHCH_3 \rightarrow [CD_3CH_2CH_2] \rightarrow CD_3+C_2H_4, \quad (11)$$

$$CD_3CHCH_3 \rightarrow D+CD_2{=}CHCH_3, \quad (12)$$

$$CD_3CHCH_3 \rightarrow H+CD_3CH{=}CH_2. \quad (13)$$

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 CD_2CHD and C_2H_4. Since C_2H_4 is formed directly in reaction (8) as well as by reaction (11), isomerization can only be detected by measuring the CD_2CHD 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[7] and by Kerr and Trotman-Dickenson.[8]

$$CH_3CHCH_3 \rightarrow [CH_3CH_2CH_2] \rightarrow CH_3+C_2H_4, \quad (14)$$

$$CH_3CHCH_3 \rightarrow H+CH_2{=}CHCH_3. \quad (15)$$

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 α 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

$$\frac{k_{10}+k_{11}}{k_{12}+k_{13}}=\frac{\frac{1}{2}k_{14}(1+\alpha)}{\frac{1}{2}k_{15}(1+\alpha)}=\frac{k_{14}}{k_{15}}$$

$$=\frac{C_2HD_3(1+1/\alpha)}{CD_2{=}CHCH_3+CD_3CH{=}CH_2}. \quad (1')$$

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 C_2HD_3/total ethylene was measured on a mass spectrometer. From Eq. (1′)

$$\frac{\text{total ethylene}}{\text{total propylene}}\,\frac{C_2HD_3(1+1/\alpha)}{\text{total ethylene}}=\frac{k_{14}}{k_{15}}. \quad (2')$$

Now, if reaction (14) proceeds directly to CH_3 and C_2H_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, α will be less than unity. Since α 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.[11] The result so obtained gives $(k_{14}/k_{15})_{\text{isom.}}$. The results are summarized in Table I.

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

$$CH_3CHCH_3 \rightarrow CH_3 + CHCH_3 \rightarrow CH_3 + CH_2{=}CH_2.$$

It is apparent that if isopropyl decomposes directly into CH_3 and ethylene as suggested by Kerr and Trotman-Dickenson,[8] 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 $CHD{=}CD_2$, and it must be admitted that small amounts of CHD_2CDHCH_3 in the original propane as well as CD_3CDHCH_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[8] obtained by measuring the ethylene 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[8] 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[7] from their study of diisopropyl ketone-d_2 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.

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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

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A variation-perturbation formulation is presented for the calculation of the electronic contribution to the rotational energy and magnetic moment of a $^1\Sigma$ 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.[1,2] Even in essentially nonmagnetic systems (e.g., $^1\Sigma$ 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,[1] recent experimental and theoretical developments suggest that detailed studies of more complex

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† Alfred P. Sloan Foundation Fellow.

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