The Barrier to Internal Rotation in Methylfluoroform

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be predictable on the basis of an electron gas. Using Pauli's well-known equation[4] for the magnetic susceptibility of an electron gas and correcting for the Landau diamagnetism[5] we predict, after correcting for diamagnetic alkali metal ions and WO_3, the values given in line 4 of Table I for the magnetic susceptibility of the tungsten bronzes per gram atom of alkali metal.

The correspondence between the observed and calculated values is remarkably good, considering that even slight binding of the free electrons to the alkali metal ion introduces a paramagnetic correction to the values calculated on the basis of completely free electrons. The large disagreement, observed in the case of the potassium bronze, may be due to the greater polarizability of the potassium ion with consequent greater binding of the free electrons. The agreement in the case of the sodium bronzes is fully as good as that found for the pure alkali metals and better than that found for a saturated solution of sodium in liquid ammonia.[6]

Further work on these and other bronzes is in progress.

We are indebted to Dr. E. O. Brimm of Linde Air Products Company for sending us samples of the yellow and blue sodium bronzes. These bronzes were prepared by reduction with tungsten of a mixture of WO_3 and Na_2WO_4. Measurements on them are included in our results.

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Chemical Reactions in a Magnetic Field

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THE possible effects of applied magnetic fields on chemical reactions have been investigated in some detail[1,2] and in general it has been concluded that such effects, if they exist at all, are not great. Bhatnagar reported that the rates of certain inorganic reactions could be altered by approximately one percent by fields of the order of 10,000 gauss. However, Schmid, Muhr, and Marek[3] have reported that when styrene was polymerized at 80°C in a field of 16,000 gauss, an eightfold reduction in rate was observed. An explanation has been suggested for this phenomenon based on an orientation by the field of the spin moments of the unpaired electrons.[4]

The experiment reported above has been reinvestigated in this laboratory and the investigation has been extended to other reactions. An electromagnet was used which could provide a field of 14,000 gauss across a 1-in. pole space. The reactions in the field took place in a flat Pyrex cell under an inert atmosphere. This cell and a control removed from the field were maintained at a temperature of 80±0.3°C in a suitable thermostat. A field of 12,000 gauss was used for all experiments reported here.

Benzoyl peroxide is an effective catalyst for the polymerization of styrene and accordingly the effect of the field on the decomposition of this substance was investigated. Two grams of the peroxide were dissolved in 100 g of toluene and the reaction was followed until the peroxide was 70 percent decomposed. No measurable effect of the field could be observed, a result which

TABLE I. The polymerization of styrene in a magnetic field of 12,000 gauss.

Time (hr.)	Percent conversion in field	Percent conversion in control
1	11.2	11.4
2	19.9	20.0
3	28.1	28.2
4	35.7	35 9

agrees with that reported recently by Leffler[5] for a field of 7518 gauss. The catalyzed polymerization was then studied using 2.00 g of peroxide per liter of styrene. The results are given in Table I. The uncatalyzed polymerization of styrene was studied under the conditions described and also in a number of experiments in which carefully purified styrene was sealed in ampoules in the absence of air. In none of these experiments on the polymerization of styrene in a field of 12,000 gauss was any measurable effect of the field observed. A similar result has recently been reported by Breitenbach and Richter.[6]

The decomposition of hydrogen peroxide in a field of 12,000 gauss was also examined and no significant effect of the field on the rate of the reaction could be detected.

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The Barrier to Internal Rotation in Methylfluoroform

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SOME uncertainty exists in published values[1-4] for the barrier to internal rotation in methylfluoroform, CH_3-CF_3. We have re-examined its infra-red spectrum, particularly the critical long wave-length region to 300 cm^{-1}. Measurements were also made of the temperature dependence of several of the lower frequency bands as an aid in frequency assignment. Possible indirect values for the torsional frequency were obtained from combination and difference bands. The corresponding barriers were then compared with the statistical values for the barrier, computed from the fundamental frequencies in conjunction with recent structural data[5-7] and the calorimetric entropy.[1] Two internally consistent sets of frequency assignments are proposed. They lead to barriers of 1740, 2000 and 3210, 2800 cal./mole; the value 3000±200 cal./mole is considered more probable.

The spectrum of the gas was observed to 400 cm^{-1} with a Perkin-Elmer 12B spectrometer The KRS-5 region from 400 to 300 cm^{-1} was run on a similar instrument at M.I.T. through the courtesy of Dr. M. Kent Wilson of Harvard and Mr. R. S. McDonald of M.I.T. The sample of methylfluoroform was furnished by Dr. A. F. Benning, du Pont and Company. The spectrum observed agrees in most regards with that reported previously.[2] The temperature dependence of absorption listed in Table I was obtained in a sealed 7-cm gas cell[8] at a room-temperature pressure of 45 cm.

The various assignments of fundamentals are given in Table II and the Raman and infra-red spectra below 1200 cm^{-1} are given in detail in Table III. Concerning the A_1 assignments, the CH_3 bending, ν_2, is 1375^{-1} in ethane[6] and 1378 cm^{-1} in methylchloroform,[9] CH_3-CCl_3. Of the two bands, 1279 and 1410 cm^{-1}, nearest these values, 1410 cm^{-1} is most likely ν_2. This leaves the 1279

TABLE I. Temperature dependence† of some infra-red bands of CH_3-CF_3.

Band cm^{-1}	Percent transmission 20°C	130°C	190°C	Assignment
818	20	26	35	⎱
829	12	13	17	fundamental
842	18	27	32	⎰
910	62	46	32	difference band
1013	19	14	12	difference band
1090	40	30	19	difference band

† Qualitative observations of the weak 541 and 732 cm^{-1} bands revealed an increase in transmission over the same temperature range, indicating that they are not difference bands.

TABLE II. Assignments of fundamental frequencies for CH_3-CF_3.

Species	Description		Reference 1	Reference 2	This research
A_1	C−H stretching	ν_1	2974 cm⁻¹	2974 cm⁻¹	2974 cm⁻¹
	CH₃ bending	ν_2	1450	1278	1410
	C−F stretching	ν_3	968	1135	1279
	C−C stretching	ν_4	829	828	829
	CF₃ bending	ν_5	603	540	605
A_2	torsion	ν_6	—	—	(172, 218)
E	C−H stretching	ν_7	3040	3040	3041
	CH₃ deformation	ν_8	1450	1412; 1450	1450
	C−F stretching	ν_9	1279	1230	1230
	CH₃ rocking	ν_{10}	1025	606	(1185, 966)
	CF₃ deformation	ν_{11}	541	968	(966, 541)
	CF₃ rocking	ν_{12}	368	368	370

cm⁻¹ band for the C−F stretching, ν_3, for which the corresponding frequencies in fluoroform,[7] CHF_3, and perfluoroethane,[10] C_2F_6, are 1209 and 1420 cm⁻¹. Similarly, for the CF_3 bending, ν_5, the assigned values in fluoroform and perfluoroethane are 509 (or 703) and 809 cm⁻¹; the strong methylfluoroform band at 605 cm⁻¹ has an attractively close value.[11]

Perhaps the least certain part of the assignment concerns the 541, 966, and 1185 cm⁻¹ bands from which the E fundamentals ν_{10} and ν_{11} must be chosen. The vibrational mode in methylchloroform equivalent to ν_{10} has been assigned as 1179 cm⁻¹, and in ethane the E_u and E_g assignments are 821.5 and 1190 cm⁻¹. While part of the absorption by methylfluoroform about 970 cm⁻¹ may be the combination 605+370 cm⁻¹, the complex band structure suggests overlapping with what must be a fundamental. If 1185 cm⁻¹ is taken as ν_{10}, then ν_{11} is 966 cm⁻¹. On the other hand, in perfluoroethane the values assigned to the E_u and E_g vibrations similar to ν_{11} are 522.5 and 620 cm⁻¹, strongly suggesting 541 cm⁻¹ as ν_{11}. The only factor against this interpretation is the uncertain band structure and weakness of the infra-red absorption

TABLE III. Assignments of frequencies below 1200 cm⁻¹ in CH_3-CF_3.

Raman[1] cm⁻¹	Reference 2	Infra-red This research	Assignment
		356 ⎱	
368 (2)		371 ⎰m	ν_{12}
		379	
541 (2s)	540	543 mw	172 + ν_{12} or ν_{11}
	593	593 ⎱	
603 (2s)	606	605 ⎰s	ν_5
	616	616	
	733?	732 w	2ν_{12}
		747 vw	ν_3−541 or 966−219
	818	818 ⎱	
829 (5s)	828	831 ⎰s	ν_4
	840	843	
	889 ⎱s		impurity?
	900 ⎰		
	910	910 w	ν_3 − ν_{12}
	953	962 ⎱	
968 (3)	964	967 ⎰vs	ν_{11} or ν_{10}, overlapped by ν_5 + ν_{12}
	971	974	
	978	980	
	1004 w		impurity?
	1013	1013 w	1185−172 or ν_3−217
1025 (2d)?		1030 vw	ν_2−ν_{12}
		1090 w	ν_8−ν_{12}
	1125 ⎱		
	1135 ⎰s		impurity
	1143		
	1177	1173 ⎱	
	1184	1187 ⎰m	ν_{10} or 966 +219
	1191	1198	

The recent structural data[5–7] give a value for Sr of 22.16 e.u. at 224 40° and 0.9330 atmos. Combining this with the previous data and using the same methods[1] for calculation, the two sets of fundamentals give statistical values of 2000 and 2800 cal./mole for the barrier. The indirectly inferred torsional frequencies of 172 and 218 cm⁻¹ yield barrier heights of 1740 and 3210 cal /mole from the relation $V_0 \cong 8\pi^2 I_A \nu_t^2 / 3^2 h$. Both methods assume the usual $(V_0/2)(1-\cos3\phi)$ potential curve.[4] Since the second assignment is considered more likely, the barrier value of 3000±200 cal./mole is preferred.

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Infra-Red Data on Epoxy Structures

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OUR interest in the identification of epoxy groups by infra-red absorption methods was initiated by our studies of the structural changes resulting from oxidation of GR-S. One of these studies was an attempt to follow the structural changes resulting from the reaction of the double bonds in GR-S with perbenzoic acid.[1] Another concerned the hydroperoxide theory of autooxidation of Gr-S and other elastomers in which the epoxy group is involved.[2]

According to the results of other investigators,[3,4] it has been shown that absorption frequencies resulting from the epoxy group in ethylene oxide occur at approximately 865 cm⁻¹, 1165 cm⁻¹, and 1265 cm⁻¹. Since these frequencies result from absorptions by relatively simple molecules, it was thought that more reference data should be obtained from more complicated hydrocarbon compounds containing the epoxy structure. Accordingly, the authors have investigated the absorption spectra of the following compounds:

propylene oxide	styrene oxide
tetramethylethylene oxide	cyclohexene oxide
trimethylethylene oxide	butadiene monoxide
isobutylene oxide	sym. dimethylethylene oxide.

Although absorption bands were found in the spectra of the above compounds at the frequencies indicated for the epoxy group in the simple ethylene oxide molecules, only the 1250 cm⁻¹ band could be identified with reasonable certainty as being characteristic of this molecular group. In the spectra of the eight compounds investigated an absorption band was consistently found in the frequency range 1240 cm⁻¹ to 1260 cm⁻¹. Although bands were found in the other spectral regions, their use for identification purposes is less certain because of the increased number of possible C−C vibrational frequencies and C−H rocking frequencies arising from these larger molecules.

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