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Ionization Potential of the Free HO2 Radical and the H – O2 Bond Dissociation Energy

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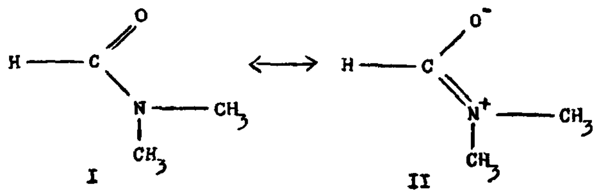
to the nitrogen atom, a chemical shift is expected between the two methyl groups in the event of restricted rotation about the C−N bond. The different fields experienced by the hydrogen atoms of the two CH_3 groups in the planar configuration as the result of different intramolecular distances and asymmetric polarization of the C−N bond would be expected to produce different magnetic shieldings of the hydrogen atoms of the two CH_3 groups and give rise to the observed chemical shift.

Restricted rotation about the C−N bond of amides is reasonable from the point of view of molecular orbital theory in that overlap is possible between the *p*-orbital of carbon and the *p*-orbital of nitrogen containing an unshared pair of electrons. The two predominant resonance structures are those given below with resonance structure II making an appreciable contribution to the electronic structure of amides.[1]



It is possible to place an upper limit on the rotational velocity about the C−N bond of N,N-dimethylamides from the observed chemical shift between the two methyl groups. The chemical shift of 6 cps between the two methyl groups indicates that these groups are exchanging positions by rotation about the C−N bond at a rate of less than $6(2\pi)=38\ \text{sec}^{-1}$. If the rate of positional exchange of the methyl groups of N,N-dimethylformamide by rotation about the C−N bond were equal to or greater than about $38\ \text{sec}^{-1}$, only a single, average methyl proton resonance located between −60 and −66 cps would be observed.[4] This low value of $38\ \text{sec}^{-1}$ at room temperature for the upper limit of the rate of rotation about C−N bonds indicates that the energy barriers for restricted rotation in amides is high.

Observation of single methyl proton resonances for N-methylformamide and N-methylacetamide indicates that only one of the two possible rotational isomers of these compounds is present. Mizushima[3] deduced the same result from analysis of the infrared and Raman spectra of N-methylacetamide.

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[1] L. Pauling, *The Nature of the Chemical Bond* (Cornell University Press, Ithaca, 1948), p. 207.

[2] S. Mizushima, *Structure of Molecules and Internal Rotation* (Academic Press, Inc., New York, 1954), pp. 139–152.

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Ionization Potential of the Free HO_2 Radical and the $H-O_2$ Bond Dissociation Energy*

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THEORETICAL estimates[1–5] of the heat evolved in the reaction $H+O_2 \rightarrow HO_2$ have ranged from 36 to 70 kcal/mole. With the mass spectrometric detection by Foner and Hudson[6] and also by Robertson[7] of the HO_2 radical in the reaction of hydrogen atoms with oxygen molecules, the actual existence of this radical was established and the possibility of directly measuring the heat of formation of HO_2 was opened. The essential data are the ionization potential of the HO_2 radical and the appearance potential of the HO_2^+ ion from H_2O_2.

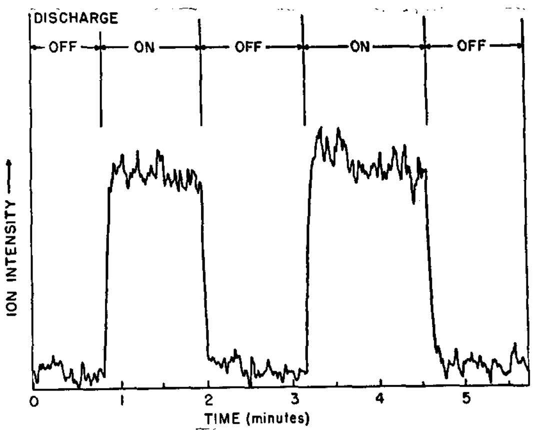

FIG. 1. HO_2 production in the reaction of H_2O_2 with discharge products of water vapor. Ion intensity of HO_2^+ recorded with 2 sec time constant at 15 volts electron energy.

The yield of HO_2 in our experiments on the reaction of atomic hydrogen with oxygen was too small to permit the determination of the HO_2 ionization potential. Recently we have obtained substantial quantities of HO_2 radicals by reacting H_2O_2 at low pressures (~0.5 mm) with the products of electrical discharges in various gases. Discharges in water vapor and hydrogen peroxide are particularly effective, probably because the OH radicals produced can react with H_2O_2 by the exothermic process:

$$OH+H_2O_2 \rightarrow HO_2+H_2O+30\ \text{kcal}. \qquad (1)$$

The reactor used in this work was similar to that described in reference 6, the major differences being that the central tube which supplied the H_2O_2 was movable and the sampling orifice was a Pyrex cone instead of a punched gold foil. The mass spectometer and the chopped molecular beam sampling system have been described.[8]

The yield of HO_2 radicals by reaction of peroxide with discharge products from water vapor is shown in Fig. 1, a recording of the mass 33 ion intensity as the discharge was alternately switched on and off. The $O^{16}O^{17}$ contribution from oxygen generated in the reaction is only 3 percent of the mass 33 ion intensity shown here. The small contribution made by HO_2^+ from H_2O_2 is evident from the ion intensity when the discharge is off (i.e., no peroxide decomposed). At 50 volts electron energy the excess HO_2^+ intensity is about 1 percent of the $H_2O_2^+$ intensity which makes the HO_2 concentration in this experiment about 0.3 percent of the gas mixture.

The initial portions of the ionization efficiency curves for the HO_2^+ ion from the radical, the HO_2^+ ion from H_2O_2, the O_2^+ ion from O_2, and the A^+ ion from argon are shown in Fig. 2. The oxy-

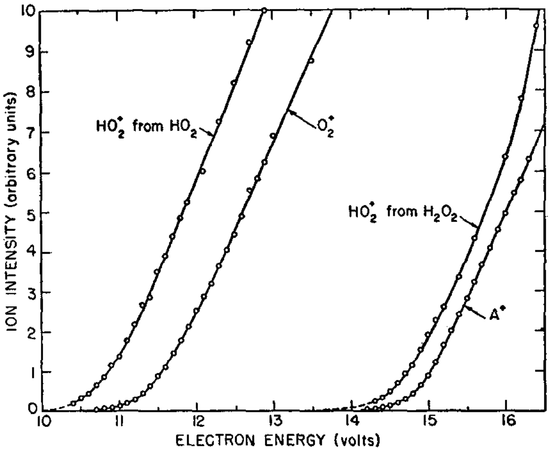

FIG. 2. Appearance potential curves of ions used to determine the heat of formation of HO_2. Voltage scale is uncorrected.

gen appearance potential curve was made, using the oxygen produced in the reaction, while the HO_2^+ curve from H_2O_2 was made with the discharge turned off. Argon was used as the standard gas (IP = 15.77 ev) to calibrate the voltage scale. The appearance potentials of the ions were determined by two objective methods: (1) Plotting log ion intensity *vs* voltage curves and determining the voltage shift required to match the curves. Various forms of this method have been used successfully by Honig,[9] Dibeler and Reese,[10] and others. (2) Removing the tail of the ionization curve due to the thermal energy spread in the electron beam by the deboltzmannization procedure of Foner, Kossiakoff, and McClure,[11] a method not too well known and inadequately described in the literature. A preliminary analysis of the data leads to the following ionization energies:

$$I(HO_2)=11.53\pm0.1 \text{ ev},$$
$$I(O_2)=12.15\pm0.1 \text{ ev},$$
$$A(HO_2) \text{ from } H_2O_2=15.41\pm0.1 \text{ ev}.$$

The difference between the energy required to produce HO_2^+ by dissociative ionization of H_2O_2 and the ionization potential of the HO_2 radical, 3.88 ev = 89.5 kcal/mole, is the energy for removal of the first hydrogen atom from H_2O_2 on the assumption of zero kinetic energy of the fragments in the process:

$$H_2O_2+e\rightarrow H+HO_2^{+}+2e. \qquad (2)$$

The empirical rule proposed by Stevenson[12] for zero kinetic energy in dissociative ionization is satisfied since $I(HO_2)<I(H)$. Using the known heat of the reaction

$$2H+O_2\rightarrow H_2O_2+136.6 \text{ kcal/mole or } 5.92 \text{ ev}$$

with our value of $D(H-HO_2)$ we obtain for the bond dissociation energy of $H-O_2$, $D(H-O_2)=2.04\pm0.1$ ev or 47 ± 2 kcal/mole.

Our value for $D(H-O_2)$ is consistent with the value reported by Robertson,[13] $D(H-O_2)=46\pm9$ kcal/mole. This agreement, however, must be considered as fortuitous since Robertson's value is derived on the assumption that $I(HO_2)\equiv I(O_2)\equiv 12.2$ ev, an estimate which is in error by 0.7 ev, and a measured value for the appearance potential of HO_2^+ from H_2O_2 of 16.1 ± 0.4 ev which is in marked disagreement with our value of 15.41 ± 0.1 ev.

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Vibrational Analysis of the Emission Spectrum of Coronene as a Forbidden Transition

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THE absorption spectrum of coronene in benzene shows a weak transition from 23 000–27 000 cm^{-1} with logϵ = 2.5, and this has been interpreted as a weakly allowed electronic transition.[1] The emission spectrum of coronene in heptane at −180°C exhibits much sharp structure,[2] and it is possible to attempt a vibrational analysis of the emission spectrum. The first emission band at 4261 A is very weak, and its intensity varies considerably in different solvents.[3] The analog of this band appears weakly at 4200 A in both the absorption and emission spectra of coronene in benzene at room temperature.[1] The vibrational analysis indicates that most of the bands in the coronene emission spectrum in frozen heptane arise from vibrational additions to the doublet at 4315–4328 A, and not from vibrational additions to the first band at 4261 A. The first band at 4261 A is therefore assigned to the 0−0 band of an electronic transition which is forbidden by symmetry. The intensity in the emission transition is due to a vibrational-electronic perturbation,[4] in which the vibrational interval from the 4261 A band to the 4315–4328 A doublet corresponds to one quantum of the vibration which allows the transition to occur.

According to the LCAO-MO calculations,[5] the highest filled MO of coronene in the electronic ground state is E_{2u}, whereas the lowest unfilled MO is E_{1g}. The lowest one-electron transition is therefore orbitally fourfold degenerate. This is exactly the situation in benzene, which also possesses D_{6h} symmetry. In benzene, electron emulsion removes the occidental fourfold degeneracy to give one degenerate E_{1u} state and two nondegenerate states, B_{1u} and B_{2u},[6] with the B_{2u} state lowest in energy. The absorption and fluorescence spectra of benzene vapor have been vibrationally analyzed,[7] and the emission spectrum arises from a one-quantum addition of an e_g^+ vibration of 606 cm^{-1} to the forbidden 0−0 band. If the lowest excited electronic singlet state of coronene is $^1B_{2u}$, and if the vibration which perturbs the ground state in the emission is also an e_g^+ vibration, then it is possible to account for the doublet nature of the bands at 4315 and 4328 A in the coronene emission spectrum. The doublet is due to removal of the degeneracy of the e_g^+ vibration by interaction of the solvent with the coronene in such a way that the sixfold axis of symmetry is destroyed. The same perturbation by the solvent also allows the 0−0 band at 4261 A to appear weakly, and this is consistent with the fact that the relative intensity of this band depends on the solvent.

TABLE I. Vibrational analysis of the emission spectrum of of coronene in heptane at −180°C.

Intensity	λ, A,[a] ±3	N, cm^{-1}, ±15	23 460-N, ±20	Assignment
vw	4261	23 460	0	$^1B_{2u}\rightarrow{}^1A_{1g}$
m	4315	23 170	290	320, e_g^+
m	4328	23 100	360	
vw	4374	22 860	600	640, a_{1g}
vs	4437	22 530	930	320, e_g^+, +640, a_{1g}
vs	4449	22 470	990	
w	4490	22 270	1190	1190, a_{1g}(?)
s, broad	4531	22 060	1400	1400, e_g^+(?)
w	4577	21 840	1620	320, e_g^+, +1320, a_{1g}
w	4595	21 760	1700	
vw	4631	21 590	1870	640, a_{1g}, +1190, a_{1g}
m	4716	21 200	2260	320, e_g^+, +640, a_{1g}, +1320, a_{1g}
m	4731	21 130	2330	
vw, broad	4833	20 680	2780	1400, e_g^+, +1320, a_{1g}
vw, broad	4898	20 410	3050	
vw	5040	19 840	3620	320, e_g^+, +640, a_{1g}, +2(1320), a_{1g}
vw	5060	19 760	3700	

[a] See reference 2.

The vibrational analysis is given in Table I. The intensity distribution in the bands is consistent with a transition which is forbidden by symmetry but which is allowed by vibrational-electronic perturbation by a degenerate vibration. Perturbations due to the solvent remove the degeneracy of the e_g^+ vibration and also allow the forbidden 0−0 band to appear weakly. The degenerate e_g^+ vibration is approximately 320 cm^{-1} in coronene, and prominent additions of 640 cm^{-1} and 1320 cm^{-1} to the e_g^+ vibration are assigned to a_{1g} vibrations. The broad, strong band at 4531 A may be due to an e_g^+ vibration of 1400 cm^{-1} which adds to the 0−0 band, and partial removal of the degeneracy by solvent perturbation would account for its breadth. A very tentative assignment of an a_{1g} 1190 cm^{-1} vibration is also proposed.

In conclusion, the vibrational analysis of the emission spectrum and the solvent effects on the emission spectrum of coronene both