Rate Constants for the Reaction of the Hydroxyl Radical with Aromatic Molecules

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From Fig. 1 the intensity ratio $3^1P/2^1P=0.22$, while from Fig. 2 the ratio $3^1S/2^1S=0.22$, background corrections having been made in both cases. The first ratio is within 5% of that obtained by Skerbele and Lassettre.[7] The second ratio cannot be checked by any previous determination, but it is obvious from the figure that the accuracy cannot be high.

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Rate Constants for the Reaction of the Hydroxyl Radical with Aromatic Molecules*

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In an investigation[1] of the pulse radiolysis of aqueous benzene solutions it was shown from spectral, kinetic, and chemical evidence that the reaction of the hydroxyl radical with benzene was that of ring addition to form the hydroxycylohexadienyl radical. This conclusion was subsequently confirmed[2] by the identification of this species from its ESR spectrum in flow experiments with aqueous benzene solutions. In the pulse radiolysis work[1] the optical absorption spectra of the $(OH)C_6H_6\cdot$ radical and other substituted cyclohexadienyl radicals were observed and the absolute rate constant for OH addition to benzene was determined.

We have extended this investigation to the determination of the absolute rate constants for the reaction of the hydroxyl radical with toluene and benzoic acid, and have repeated the determination for benzene in acid solution. All experiments were done at *p*H 3 in de-aerated aqueous solutions acidified with perchloric acid. The experimental techniques have been described.[1,3] The reaction with benzene was monitored at 313 mμ, the absorption maximum, and with toluene at 313 and 308 mμ, near the reported[1] maximum in the absorption spectrum. The reaction with benzoic acid was monitored at several wavelengths from 313 to 360 mμ, but principally at 340 and 350 mμ. The transient absorption in aqueous benzoic acid solution has a maximum at 350 mμ with a band half-width of about 25 mμ. In all experiments the monitoring light had a bandwidth of 2.4 mμ as determined by the slit-width of the monochromator used.

In the case of the two volatile compounds, benzene and toluene, the reaction cell had a negligible gas volume compared to the liquid volume in order to minimize any uncertainty in the concentration of the reactants. The benzene concentration was checked in the master solutions as well as after the runs by absorption spectrophotometry.[4] The uncertainty in the concentration may be as much as 10% to 15%. The benzoic acid concentration was also checked by absorption spectrophotometry[5]; the uncertainty here is very small. The range of concentration covered was: benzene $(0.8 \text{ to } 3.5)\times10^{-4}M$; toluene $(1.9 \text{ to } 2.5)\times10^{-4}M$; benzoic acid $(1.6 \text{ to } 3.5)\times10^{-4}M$. The ratio of the initial concentration of hydroxyl radical to that of the aromatic molecule was 0.02 or less.

The formation rate curves for all three solutions were first order. The absolute rate constants obtained at 25°C are:

	Reaction	$k(M^{-1}\text{ sec}^{-1})$
(1)	$OH+C_6H_6$	$(3.3\pm0.8)\times10^9$
(2)	$OH+C_6H_5CH_3$	$(3.0\pm0.7)\times10^9$
(3)	$OH+C_6H_5COOH$	$(2.1\pm0.3)\times10^9$

Since the hydroxyl radical is the more rapidly diffusing reactant, and the reaction in all three cases is primarily ring addition, it would be expected that the three rate constants be comparable, as is indeed the case. The fact that $k_2\cong k_1$ is consistent with the earlier spectral observations,[1] which indicated that ring addition, in the case of toluene, is predominant over side chain abstraction, although there may be a small contribution[6] to k_2 from the benzyl formation reaction. Thus,

$$k_2=k_{\text{add.}}+k_{\text{abstr.}}, \quad \text{with} \quad k_{\text{add.}}\gg k_{\text{abstr.}}.$$

In the radiation chemistry of aqueous benzoic acid solutions, both dicyclic products and hydroxylated benzoic acids (in all three ring positions) are found.[7–11] The evidence is thus consistent with a reaction intermediate containing the hydroxyl radical. It should, however, be stressed that, judging from the results for aqueous benzene,[1,12] the relationship between the primary organic free radicals formed and the final stable products is quite complex and by no means fully understood.

The value for k_1 differs slightly from the earlier value[1] for OH addition to both benzene and benzene-d_6, and is considered to be the more accurate value because of greater certainty in the benzene concentration.

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Rotational Relaxation in Carbon Dioxide and Nitrous Oxide

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RECENTLY much interest has been shown, both theoretically and experimentally, in the rotational relaxation of polyatomic molecules. The rotational relaxation theories of Parker,[1] Wang Chang and Uhlenbeck,[2] and Sather and Dahler[3] suggest that the rotational energy levels of linear molecules are excited more efficiently than those of spherically symmetric molecules. This is broadly confirmed by the ultrasonic measurements of Holmes, Jones, and Pusat[4] and by the thermal transpiration measurements of O'Neal and Brokaw.[5] Since the carbon dioxide and nitrous oxide molecules are linear, it is expected that they should have efficient rotational relaxation processes which would have an appreciable effect on sound propagation only at high frequency/pressure ratios. Further, vibrational relaxation of both these molecules occurs at relatively low f/p ($\sim$20 kc/sec·atm for CO_2 and $\sim$250 kc/sec·atm for N_2O) so that the effects of this above 10 Mc/sec·atm are negligibly small thus facilitating the analysis of the results. Zartman[6] has measured sound absorption up to 85 Mc/sec·atm in carbon dioxide. Below 30 Mc/sec·atm his absorption measurements are in good agreement with the combined theoretical vibrational relaxation–viscothermal absorption. At higher f/p the measurements are less accurate, but suggest that there might be an excess absorption over the viscothermal, which could be due to rotational relaxation.

In this letter a detailed investigation of sound propagation in carbon dioxide and nitrous oxide at high f/p is reported. The nitrous oxide (British Oxygen, 99.9%) was dried over phosphorous pentoxide and further purified by triple distillation at liquid-nitrogen temperature. No attempt was made to further purify the carbon dioxide (British Oxygen, 99.99%). Both gases were dried continuously over phosphorous pentoxide throughout the measurements. Measurements at 25°C were made in the range 10–1000 Mc/sec·atm with condenser transducers at a frequency of 100 kc/sec and pressures down to 0.05 mm Hg. The viscothermal effects were estimated with the Burnett theory as described in Holmes, Jones, and Pusat.[4] In both gases the dispersion measurements were in agreement with the Burnett theory but the measured absorption showed a slight excess throughout the whole f/p range. This excess was interpreted as being due to rotational relaxation and was analyzed with the usual expressions (Herzfeld and Litovitz[7]). The total viscothermal–relaxation effects were calculated with the expressions suggested by Greenspan.[8] The theoretical curves showing best agreement with the absorption measurements suggest that Z_r (approximately the number of collisions for rotational equilibrium to be established) is $\sim$1.3 to 2 collisions for both carbon dioxide and nitrous oxide. The effect of such a relaxation process on the total dispersion is small and the combined relaxation–viscothermal dispersion curve lies within the scatter of the experimental points.

The above collision numbers are in agreement with theoretical values for prolate spherocylindrical molecules. Sather and Dahler[3] have shown that the most important parameter in determining Z_r for such molecules is $\alpha = mL^2/8I$, where m is the molecular mass, L is the cylinder length, and I is the moment of inertia. For carbon dioxide $\alpha = 0.69$ and for nitrous oxide $\alpha = 0.73$, from which $Z_r = 3.2 - 3.4$. If the attractive part of the intermolecular potential is taken into account (Sather and Dahler[9]), the Z_r values are reduced to 2.5 collisions, in agreement with the experimental values.

The present collision numbers are also in agreement with values obtained with other experimental techniques. Thermal transpiration measurements by O'Neal and Brokaw[5] in carbon dioxide gave $Z_r = 2.4$, while the shock-tube measurements of Andersen and Hornig[10] indicate a small collision number, probably less than 1.5 collisions for both gases.

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