

to give a common basis for discussion, the qualitative observations that triplet methylene does not abstract deuterium from methane- $d_4$ <sup>7</sup> and most probably does not abstract hydrogen from neopentane<sup>8</sup> are corroborated by the BEBO calculations.

The observations that triplet methylene abstracts hydrogen predominantly from the secondary or tertiary positions in alkanes and abstracts from the allyl position in butene-2, very nearly to the exclusion of abstraction from the vinyl position,<sup>23</sup> may be understood in terms of competition between abstraction and self-association of triplet methylene or its reactions with other radicals. Using the "threshold" rate constant criterion of  $10^4 \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ , the preceding observations are predicted by these BEBO calculations. While the above considerations are necessarily qualitative because the

calculated rate constants are only approximate, they are capable of rationalizing the results of recent work on the reactivity of triplet methylene and thus (hopefully) the empiricism of the present calculations can be justified in the light of whatever insight into triplet methylene reactivity they have provided. A more detailed understanding of triplet methylene reactivity, as well as an adequate test of the applicability of the BEBO method to hydrogen transfer to triplet methylene, must await experimental values of rate constants and Arrhenius parameters.

*Acknowledgment.* The author thanks Mrs. Marianne Litzinger for writing the computer program, and Mr. William Chin for assistance with the computations.

(23) T. W. Eder, Ph.D. Thesis, University of Minnesota, 1969.

## Steady-State Intermediate Concentrations and Rate Constants. Some HO<sub>2</sub> Results

by A. A. Westenberg\* and N. deHaas

*Applied Physics Laboratory, The Johns Hopkins University, Silver Spring, Maryland 20910 (Received December 21, 1971)*

*Publication costs assisted by the Applied Physics Laboratory*

The equations governing the decay of H atoms in the H-O<sub>2</sub>-M system are derived, using the steady-state approximation for the concentration of the intermediates HO<sub>2</sub>, O, and OH. The validity of this approximation is demonstrated experimentally for a room temperature fast flow system containing a trace of H in an inert carrier (Ar or He) with an excess of O<sub>2</sub> added through a movable injector. Measurement of the absolute concentrations of H and of steady-state OH and O (by esr spectroscopy) allows the relative rates of reaction by the three paths  $\text{H} + \text{HO}_2 \xrightarrow{k_2} \text{H}_2 + \text{O}_2$ ,  $\text{H} + \text{HO}_2 \xrightarrow{k_3} \text{OH} + \text{OH}$ , and  $\text{H} + \text{HO}_2 \xrightarrow{k_4} \text{H}_2\text{O} + \text{O}$  to be determined. The rate constants  $k_2/k_3/k_4$  have the respective fractional values 0.62:0.27:0.11. From the H decay rates the rate constant  $k_1$  for  $\text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M}$  is then determined to be  $6.8 \pm 1.0 \times 10^{15} \text{ cm}^3 \text{ mol}^{-2} \text{ sec}^{-1}$  for M = Ar or He, in excellent agreement with two previous literature values. The analysis is then extended to include the case where an excess of CO (compared to H) is also added to the H-O<sub>2</sub>-M system in order to evaluate the possible significance of the reaction  $\text{CO} + \text{HO}_2 \xrightarrow{k_7} \text{CO}_2 + \text{OH}$ . It is shown that the ratio  $k_7/k_3$  may be evaluated by two methods. In method I only (HO<sub>2</sub>) is assumed to be in steady state (a reasonable assumption), and a number of runs give an average value  $k_7/k_3 = 0.06 \pm 0.02$ . Method II assumes (OH) and (O) to be at their steady-state values also (possibly less reasonable), which yields a considerably higher  $k_7/k_3$ . In either case, the appreciable contribution of  $k_7$  is incompatible with a large activation energy for this reaction, a result which (it is argued) is not surprising.

### I. Introduction

The ubiquitous radical HO<sub>2</sub> is one of those whose reaction rates with other species are usually "estimated," there being practically no reliable measurements available. A direct mass spectrometer monitoring of the second-order decay of HO<sub>2</sub> in a linear flow system permitted Foner and Hudson<sup>1</sup> to evaluate the rate constant for  $\text{HO}_2 + \text{HO}_2 \rightarrow \text{H}_2\text{O}_2 + \text{O}_2$ , although there was apparently a complicating wall reaction as well. This is the only direct measurement of an HO<sub>2</sub> reaction of

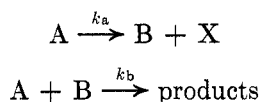
which we are aware. Other data which have been reported involve indirect experiments of various kinds, usually of rates of HO<sub>2</sub> reactions relative to others. Some of these have been reviewed.<sup>2,3</sup>

(1) S. N. Foner and R. L. Hudson, *Advan. Chem. Ser.*, **No. 36**, 34 (1962).

(2) F. Kaufman, *Ann. Geophys.*, **20**, 106 (1964).

(3) D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, *High Temperature Reaction Rate Data Report No. 3*, Leeds University (1969).

The  $\text{HO}_2$  situation is typical of reactive intermediates which are difficult to prepare in a controlled fashion, and even more difficult to measure. The relatively recent advent of esr spectroscopy as a quantitative detector of a number of gas phase free radicals offers the potential, at least, of an approach to such rate measurements which has received relatively little attention, although the principle has been used.<sup>2</sup> As the simplest possible example, consider the consecutive competitive pair of reactions



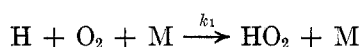
where B is a free-radical intermediate. If conditions are such that the steady-state approximation is applicable to B, i.e.,  $k_b(\text{A})_0 \gg k_a$  and the reaction time is longer than the induction time, then the radical concentration is given by the well-known relation  $(\text{B}) = k_a/k_b$ . The degree to which this approximation is approached in various cases has been discussed analytically by Giddings and Shin.<sup>4</sup> Thus if the steady-state (B) can be measured and  $k_a$  is known, the rate constant  $k_b$  can be determined. Measurement of (B) allows the evaluation of the relative rate  $k_a/k_b$  at least.

In the case of  $\text{HO}_2$ , esr detection in the gas phase has not yet been feasible (nor is it likely to become so). Nevertheless, by measuring certain other steady-state species it is possible to make relative measurements of some important  $\text{HO}_2$  rates, as is shown in the present paper.

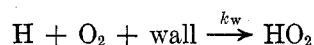
All numerical rate constants quoted are in  $\text{cm}^3\text{-mole-sec}$  units.

## II. Steady-State Analysis

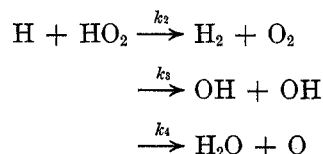
For present purposes, a clean method of generating  $\text{HO}_2$  at room temperature is the reaction



There may also be a heterogeneous contribution



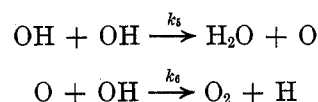
which was suggested in the work of Clyne and Thrush<sup>5</sup> and confirmed here. The  $\text{HO}_2$  concentration available in this way is kept low<sup>6</sup> by the subsequent steps



In the presence of relatively large (H) these reactions will predominate in consuming  $\text{HO}_2$ , so that reaction of  $\text{HO}_2$  with either O or OH, or with itself, will be negligible. This has been discussed in detail previously.<sup>5</sup> Wall loss of  $\text{HO}_2$  is also reported<sup>7</sup> to be

negligible on a boric acid treated surface such as used in the experiments to be described.

The OH and O formed will undergo the reactions



which complete the mechanism if no further substances are added.

Let us consider the case where  $\text{O}_2$  is in large excess compared to all other reactive species so that both  $(\text{O}_2)$  and (M) may be taken to be constant (in a reactor at constant temperature and pressure). We now apply the steady-state approximation to each of the intermediates  $\text{HO}_2$ , O, and OH in turn. Whether or not this is justified in each case is discussed later. Certainly a steady-state  $(\text{HO})_2$  should be attained first, since the slow initiating reactions are followed by reactions 2, 3, and 4 which ought to be very fast, and the required condition  $k(\text{H})_0 \gg [k_1(\text{M}) + k_w](\text{O}_2)$  should obtain after a very short time ( $k = k_2 + k_3 + k_4$ ). The steady-state condition gives

$$(\text{HO}_2)_s = [k_1(\text{M}) + k_w](\text{O}_2)/k \quad (1)$$

$$(\text{OH})_s = \left\{ \frac{[k_1(\text{M}) + k_w](2 - k_4/k_3)(\text{H})(\text{O}_2)}{3k_5(1 + k_4/k_3)(1 + x)} \right\}^{1/2} \quad (2)$$

$$(\text{O})_s = \frac{1}{k_6} \left\{ \frac{4k_5[k_1(\text{M}) + k_w](1 + k_4/k_3)(\text{H})(\text{O}_2)}{3(2 - k_4/k_3)(1 + x)} \right\}^{1/2} \quad (3)$$

where the definition  $x = k_2/(k_3 + k_4)$  has been used, following Clyne and Thrush.<sup>5</sup> The expression for H decay normalized to some reference value  $(\text{H})_0$  then becomes

$$\frac{d \ln [(\text{H})_0/(\text{H})]}{dt} = 2(\text{O}_2)[k_1(\text{M}) + k_w] \left[ \frac{3x + 2}{3x + 3} \right] \quad (4)$$

These relations may be combined in several ways which will be useful. Dividing (2) by (3) yields

$$\frac{(\text{OH})_s}{(\text{O})_s} = \frac{k_6 \left[ 2 - k_4/k_3 \right]}{2k_5 \left[ 1 + k_4/k_3 \right]} \quad (5)$$

which permits  $k_4/k_3$  to be determined from a measurement of the steady-state ratio  $(\text{OH})_s/(\text{O})_s$  and knowledge of  $k_6/k_5$ . Then the product

$$(\text{OH})_s(\text{O})_s = \frac{2[k_1(\text{M}) + k_w](\text{H})(\text{O}_2)}{3k_6(1 + x)} \quad (6)$$

and the quantity defined from eq 4

(4) J. C. Giddings and H. K. Shin, *Trans. Faraday Soc.*, **57**, 468 (1961).

(5) M. A. A. Clyne and B. A. Thrush, *Proc. Roy. Soc., Ser. A*, **275**, 559 (1963).

(6) S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **36**, 2681 (1962).

(7) I. A. Vardanyan, G. A. Gachyan, and A. B. Nalbandyan, *Dokl. Akad. Nauk SSSR*, **193**, 123 (1970); *Engl. Trans.*, **193**, 498 (1970).

$$B_M = \frac{1}{(O_2)} \frac{d \ln [(H)_0/(H)]}{dt} = 2[k_1(M) + k_w] \left[ \frac{3x+2}{3x+3} \right] \quad (7)$$

may be combined to give

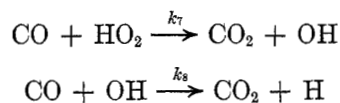
$$k_6(3x+2) = B_M \left\{ \frac{[(H)/(O_2)]}{[(OH)_s/(O_2)][(O)_s/(O_2)]} \right\} \quad (8)$$

where  $B_M$  denotes the experimental H decay slope at a given value of (M) and  $(O_2)$ .  $x$  may thus be evaluated from a measured  $B_M$ , the bracketed quantity in eq 8, and knowledge of  $k_6$ . Finally, the slope of a plot of  $B_M$  vs. (M) gives

$$\frac{dB_M}{d(M)} = 2k_1 \left[ \frac{3x+2}{3x+3} \right] \quad (9)$$

which allows  $k_1$  to be found once  $x$  is known, and then the wall constant  $k_w$  from eq 7.

Now consider what happens when another reactant, say CO, is added to the reacting mixture in amounts large enough compared to (H) so that its concentration may also be taken constant, along with  $(O_2)$  and (M). The termolecular reaction  $H + CO + M \rightarrow HCO + M$  will not occur appreciably in competition with reaction 1 if  $(O_2)$  and (CO) are roughly comparable, since it has a rate constant more than two orders of magnitude less<sup>8</sup> than  $k_1$ . The only other possible additional reactions are



Reaction 8 is sure to be important, since it is known<sup>9,10</sup> to be reasonably fast ( $k_8 \simeq 10^{11}$ ) at room temperature. Reaction 7 is of greatest present interest, and the assessment of its possible importance was one of the main reasons for undertaking this work.

Proceeding with a steady-state analysis as before, if  $HO_2$  is in a steady state

$$(HO_2)_s = \frac{[k_1(M) + k_w](O_2)(H)}{k(H) + k_7(CO)} \quad (10)$$

which may be used in the sum of the (H) and (OH) rates to give

$$\frac{d(H)}{dt} + \frac{d(OH)}{dt} = -2[k_1(M) + k_w](H)(O_2) \times \left[ \frac{k_2 + k_4}{k + k_7(CO)/(H)} \right] - 2k_5(OH)^2$$

or in integrated form between times  $t_i$  and  $t_j$

$$\begin{aligned} \frac{(H)_i}{(O_2)} - \frac{(H)_j}{(O_2)} + \frac{(OH)_i}{(O_2)} - \frac{(OH)_j}{(O_2)} = \\ 2[k_1(M) + k_w] \left[ \frac{k}{k_3} - 1 \right] \times \\ (O_2) \int_{t_i}^{t_j} \frac{[(H)/(O_2)] dt}{k/k_3 + k_7(CO)/k_3(H)} + \\ 2k_5(O_2) \int_{t_i}^{t_j} [(OH)/(O_2)]^2 dt \quad (11) \end{aligned}$$

This expression will be useful later.

If both OH and O are in steady state *in addition* to  $HO_2$ , setting their rates equal to zero and using (10) leads to

$$\frac{k_7}{k_3} = \frac{(1 + k_4/k_3)(1 + x)G - (2 - k_4/k_3)}{(1 - G)(CO)/(H)} \quad (12)$$

where the quantity  $G$  is defined by

$$G = \frac{(OH)_s/(O_2)}{k_1(M) + k_w} \left[ 3k_5 \frac{(OH)_s}{(H)} + k_8 \frac{(CO)}{(H)} \right] \quad (13)$$

Use of eq 12 to determine  $k_7/k_3$  involves a higher level of assumption than eq 11, and results by both methods will be compared.

### III. Experimental Section

A fixed cavity-movable injector discharge flow apparatus essentially as described previously<sup>11</sup> was employed. All sections of the reactor downstream of the discharge were coated with  $H_3BO_3$  to reduce wall losses. H atoms were furnished from a trace of  $H_2$  added to the argon or helium carrier upstream of the discharge, which dissociated the  $H_2$  nearly completely.  $O_2$  was metered into the movable injector in large excess compared to H for generation of  $HO_2$ , and CO was metered and mixed with the  $O_2$  before entering the injector for the runs where it was desired. Procedures for metering flows, measuring pressure, etc., have all been described. All runs were performed at room temperature.

Two significant departures from our previous technique deserve special comment. The first concerns the method of measuring absolute OH concentrations. The basic principle as described<sup>12</sup> is to compare the integrated OH signal with that of a known pressure of NO, the latter being usually accomplished by a separate filling of the reactor with pure NO. In the present

(8) T. Hikida, J. A. Eyre, and L. M. Dorfman, *J. Chem. Phys.*, **54**, 3422 (1971).

(9) G. Dixon-Lewis, W. E. Wilson, and A. A. Westenberg, *ibid.*, **44**, 2877 (1966).

(10) N. R. Greiner, *ibid.*, **46**, 2795 (1967).

(11) A. A. Westenberg and N. deHaas, *ibid.*, **47**, 1393 (1967).

(12) A. A. Westenberg, *ibid.*, **43**, 1544 (1965). It should be noted that an error of a factor of 2 in deriving the NO and OH matrix elements in this paper has been pointed out by W. H. Breckenridge and T. A. Miller, *ibid.*, **56**, 475 (1972). The error cancels out when the OH/NO calibration relations are computed, so that the  $Q_{OH}$  values in Table III of this reference are correct. The factor  $Q_0$  for electron concentrations should be divided by 2, however.

case, since an appreciable concentration of  $O_2$  always existed in the reactor anyway, it was much more convenient (and probably more reliable) to measure the OH intensity relative to that of the  $O_2$  signal, and then use an empirical cavity factor to convert from the magnetic dipole  $O_2$  case to the electric dipole NO and OH transitions. This empirical factor was determined by measuring the first moment<sup>13</sup>  $I_{NO}$  (using line a of the NO spectrum in our nomenclature<sup>12</sup>) with a pressure  $P_{NO}$  of pure NO in the reactor tube passing through the cavity and a given set of instrumental variables, and  $I_{O_2}$  at  $P_{O_2}$  (using line E of the  $O_2$  spectrum<sup>13</sup>) with pure  $O_2$  at the same instrumental settings. The desired factor was then given by  $(I_{NO}/I_{O_2})(P_{O_2}/P_{NO})$ , which was, of course, specific to our cavity<sup>14</sup> (TE<sub>011</sub>) and flow tube. In this way the desired ratios  $(OH)/(O_2)$ , as well as  $(H)/(O_2)$ , could both be found from the same calibration measurement on the known  $O_2$  concentration present during a kinetic run. The  $(H)/(O_2)$  did not, of course, require the empirical factor since H exhibits magnetic dipole transitions and thus responds to the same geometry of microwave field vector as  $O_2$ .

The other detail of technique worth noting was that some of the steady-state O concentrations to be measured were so low as to make integrated intensities difficult to obtain reliably. In these cases, a separate O signal was obtained with a larger concentration furnished by admitting some  $O_2$  to the carrier flow upstream of the discharge (which did not otherwise perturb the pressure or overall mixture in the cavity appreciably), and the desired low (O) was evaluated from the moment of this larger (O) and the ratio of signal peak heights, the latter being much easier to measure at very low signal/noise. Since the line widths were identical in the two cases, this scaling procedure was perfectly valid. The same technique was used for low (OH) in some of the runs with CO present, a larger OH signal for integration being obtained with the CO turned off.

#### IV. Results and Discussion

The H- $O_2$ -M system with no other added species is considered first. The analysis leading to eq 1-9 was based on the steady-state approximation applying to all three species  $HO_2$ , OH, and O. Equation 4 then predicts a straightforward, pseudo-first-order, logarithmic decay of (H) at any fixed pressure, *i.e.*, (M), and eq 2 predicts that  $(OH)_s^2 \propto (H)$ . The latter is a much more sensitive test of the steady-state condition, since reactions 1-4 dominate the (H) decay process and a steady state for  $(HO_2)$  alone gives essentially a linear logarithmic (H) decay behavior. By proper choice of flows and total pressure it was possible to attain reasonably well the desired conditions where  $(OH)_s^2 \propto (H)$  and examples are given in Figure 1. By increasing the linear flow velocity it was always possible to reach a regime where the available reaction

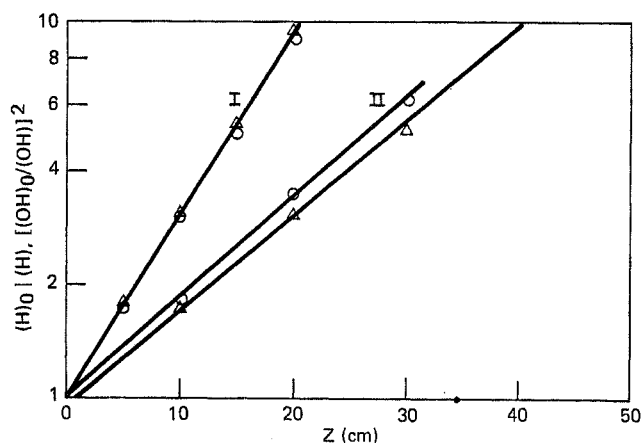


Figure 1. Examples of (H) and  $(OH)^2$  decay down flow tube, showing that  $(OH)^2 \propto (H)$ :  $\circ$ ,  $(H)_0/(H)$ ;  $\Delta$ ,  $[(OH)_0/(OH)]^2$ . Run I:  $P = 2.73$  Torr,  $v = 270$  cm/sec,  $(O_2) = 1.69 \times 10^{-8}$  mol/cm<sup>3</sup>. Run II:  $P = 1.60$  Torr,  $v = 425$  cm/sec,  $(O_2) = 2.34 \times 10^{-8}$  mol/cm<sup>3</sup>.  $z = 0$  was 16 cm from the cavity center.

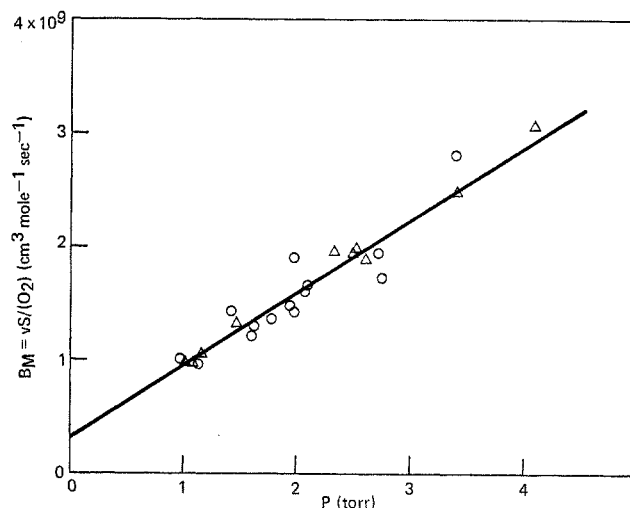


Figure 2. Plot of  $vS/(O_2)$  against total pressure in reactor:  $S = d \ln [(H)_0/(H)]/dz$ ;  $\circ$ , M = argon;  $\Delta$ , M = helium.

time was insufficient for attainment of  $(OH)_s$ , and the (OH) could even be observed to increase while (H) was decreasing. Absolute values of (H), (OH), and (O) were only measured when the condition  $(OH)_s^2 \propto (H)$  was shown to exist.

Letting the H decay slope  $S = d \ln [(H)_0/(H)]/dz$ , eq 7 requires that a plot of  $BM = vS/(O_2)$  against (M) be linear, where  $v$  is the linear flow velocity. The results of a large number of such runs are plotted in Figure 2. The experimental slope  $S_e$  in each case was corrected for longitudinal diffusion<sup>11</sup> by the relation  $S = S_e(1 + S_e D_H/v)$ , where  $D_H$  is the diffusion coefficient of H in the carrier gas (Ar or He) at the pressure of the experiment. The corrections in Ar and He

(13) A. A. Westenberg and N. deHaas, *J. Chem. Phys.*, **40**, 3087 (1964).

(14) A. A. Westenberg and N. deHaas, *ibid.*, **43**, 1550 (1965).

**Table I:** H Decay Slopes ( $S$ ) and Steady State (OH)<sub>s</sub> and (O)<sub>s</sub> Data (at  $z = 0$ ) Combined According to Eq 7 and 8

$P$ , Torr	$v$ , cm/sec	$S$ , cm <sup>-1</sup>	$B_M$ , cm <sup>3</sup> mol <sup>-1</sup> sec <sup>-1</sup> × 10 <sup>8</sup>	(H) (O <sub>2</sub> ) × 10 <sup>-4</sup>	(OH) <sub>s</sub> (O <sub>2</sub> ) × 10 <sup>-4</sup>	(O) <sub>s</sub> (O <sub>2</sub> ) × 10 <sup>-4</sup>	(OH) <sub>s</sub> (O) <sub>s</sub>	$B_M[(H)/(O_2)]$ [(OH) <sub>s</sub> /(O <sub>2</sub> )] [(O) <sub>s</sub> /(O <sub>2</sub> )] × 10 <sup>14</sup>
2.50 <sup>a</sup>	320	0.145	19.2	107	10.3	1.29	7.98	1.55
2.62 <sup>a</sup>	300	0.161	18.9	68	8.9	1.40	6.38	1.03
2.33 <sup>a</sup>	330	0.136	19.6	163	13.8	1.67	8.26	1.39
2.07 <sup>b</sup>	275	0.103	16.1	266	14.8	2.36	6.27	1.23
2.73 <sup>b</sup>	270	0.122	19.4	241	16.6	2.49	6.67	1.13
1.60 <sup>b</sup>	425	0.067	12.1	210	11.7	1.89	6.19	1.15
2.11 <sup>b</sup>	340	0.078	16.6	375	17.1	2.39	7.15	1.52
Av								7.0 ± 0.8      1.3 ± 0.2

<sup>a</sup> Helium carrier. <sup>b</sup> Argon carrier;  $B_M = vS(O_2)$ .

never exceed 12 and 24%, respectively. As Figure 2 demonstrates, there is no distinction between the data with  $M = \text{Ar}$  or  $M = \text{He}$ , a conclusion previously noted by Clyne and Thrush<sup>5</sup> and in some earlier results from this laboratory.<sup>15</sup> (The latter work over a smaller pressure range did not show the finite intercept indicating a second-order wall term clearly apparent in Figure 2.)

The slope in Figure 2 gives a value

$$2k_1(3x + 2)/(3x + 3) = 1.20 \pm 0.05 \times 10^{16} \text{ cm}^6 \text{ mol}^{-2} \text{ sec}^{-1}$$

and the intercept is

$$2k_w(3x + 2)/(3x + 3) = 3.2 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

Equations 5 and 8 were then applied to a number of runs in which integrated intensities were measured to determine (H)/(O<sub>2</sub>), (OH)<sub>s</sub>/(O<sub>2</sub>), and (O)<sub>s</sub>/(O<sub>2</sub>) at a given injector position ( $z = 0$ ). The results are summarized in Table I. It is seen that the quantities in the final two columns are reasonably constant as predicted, and we get

$$\frac{k_6}{2k_5} \left[ \frac{2 - k_4/k_3}{1 + k_4/k_3} \right] = 7.0 \pm 0.8$$

$$k_6(3x + 2) = 1.3 \pm 0.2 \times 10^{14} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$$

To proceed further with these basic experimental data, we need first a value for  $k_6$ . For this we prefer the recent work from this laboratory<sup>16</sup> which gave  $k_6 = 1.9 \pm 0.2 \times 10^{13} \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$  at room temperature. (Other literature values<sup>2,5,17</sup> are in the range  $3 \pm 1 \times 10^{13}$ .) With the mean deviation shown, the above value for  $k_6(3x + 2)$  yields  $x = 1.6 \pm 0.3$ . With  $x$  thus determined, the basic data then give  $k_1 = 6.8 \pm 1.0 \times 10^{15} \text{ cm}^6 \text{ mol}^{-2} \text{ sec}^{-1}$  (for  $M = \text{Ar}, \text{He}$ ), and also  $k_w = 1.8 \times 10^8 \text{ cm}^3 \text{ mol}^{-1} \text{ sec}^{-1}$ . The latter is, as noted earlier, specific to the present apparatus and of no particular significance, except that it is needed in analyzing the data obtained later.

The remaining data require the ratio  $k_6/k_5$  to extract a value for  $k_4/k_3$ . Since there are no direct data on the

ratio  $k_6/k_5$  we must use the individual  $k_6$  and  $k_5$ , with the source of the former noted above. For  $k_5$  the situation is not as well defined. There are three values in the literature obtained from careful fast flow experiments, i.e.,  $k_5 = 0.5, 0.8$ , and  $1.5 \times 10^{12}$  (from ref 17, 2, and 9). The first value was obtained after quite a sizable correction for a first-order wall loss of OH which was not observed in the other two experiments. In any case,  $k_5$  seems uncertain by at least a factor of 2 (and perhaps 3). Exercising the privilege of personal bias and using the value  $k_5 = 1.5 \times 10^{12}$ , the present basic data give  $k_4/k_3 = 0.39 \pm 0.06$ , where the indicated error represents simply the mean deviation of the experimental (OH)<sub>s</sub>/(O)<sub>s</sub> from which  $k_4/k_3$  was derived *via* eq 5. The experimental data and the results derived from them are summarized in Table II.

In comparing these results with others available in the literature we note first that our value of  $1.20 \times 10^{16}$  for  $2k_1(3x + 2)/(3x + 3)$  is in near-perfect agreement with the  $1.26 \times 10^{16}$  reported by Clyne and Thrush,<sup>5</sup> which should be the case since this quantity reflects simply the basic H decay slope as a function of (M). They also derived a value of  $x = 0.5 \pm 0.2$  by an entirely different method than ours, namely, by measuring the ratio of H<sub>2</sub>O formed to H consumed, which can be shown to equal  $(3x + 2)^{-1}$  if HO<sub>2</sub>, OH, and O are in steady state. Since their value of  $x$  was based on only three estimates of this quantity, requiring a difficult H<sub>2</sub>O measurement, the fact that it is in poor agreement with our  $x = 1.6$  is not too disturbing. The latter value would appear more reliable. Bennett and Blackmore<sup>18</sup> have estimated  $x$  to be 0.5–1.0, again with considerable uncertainty.

The  $k_1$  extracted is not very sensitive to the  $x$  value, and our  $k_1 = 6.8 \pm 1.0 \times 10^{15}$  agrees well with Clyne

(15) A. A. Westenberg, J. M. Roscoe, and N. deHaas, *Chem. Phys. Lett.*, **7**, 597 (1970).

(16) A. A. Westenberg, N. deHaas, and J. M. Roscoe, *J. Phys. Chem.*, **74**, 3431 (1970).

(17) J. E. Breen and G. P. Glass, *J. Chem. Phys.*, **52**, 1082 (1970).

(18) J. E. Bennett and D. R. Blackmore, "Thirteenth Symposium on Combustion," The Combustion Institute, Pittsburgh, Pa., 1971, p 51.

**Table II:** Results Derived from Steady-State Analysis of H-O<sub>2</sub>-M System (M = Ar, He)

Quantity	Value	Remarks
Basic Data		
$k_6(3x + 2)$	$1.3 \pm 0.2 \times 10^{14}$ (cm <sup>3</sup> mol <sup>-1</sup> sec <sup>-1</sup> )	From data of Table I and eq 8
$2k_1(3x + 2)/(3x + 3)$	$1.20 \pm 0.05 \times 10^{16}$ (cm <sup>6</sup> mol <sup>-2</sup> sec <sup>-1</sup> )	From data of Figure 2 and eq 9
$\frac{k_6(2 - k_4/k_3)}{2k_5(1 + k_4/k_3)}$	$7.0 \pm 0.8$	From data of Table I and eq 5
Derived Data		
$x = k_2/(k_3 + k_4)$	$1.6 \pm 0.3^a$	Uses $k_6 = 1.9 \pm 0.2 \times 10^{13}$
	0.8	Uses $k_6 = 3 \times 10^{13}$
$k_1$	$6.8 \pm 1.0 \times 10^{15}^a$	Uses $x = 1.6 \pm 0.3$
	$7.3 \times 10^{15}$ (cm <sup>6</sup> mol <sup>-2</sup> sec <sup>-1</sup> )	Uses $x = 0.8$
$k_4/k_3$	$0.39 \pm 0.06^a$	Uses $k_6/k_5 = 19/1.5 = 12$
	0.76	Uses $k_6/k_5 = 30/1.5 = 20$
	0.89	Uses $k_6/k_5 = 19/0.8 = 24$
	1.18	Uses $k_6/k_5 = 30/0.8 = 37$
$k_2/k, k_3/k, k_4/k$	$0.62, 0.27, 0.11^a$	Uses $x = 1.6, k_4/k_3 = 0.39$
	$0.44, 0.32, 0.24$	Uses $x = 0.8, k_4/k_3 = 0.76$
	$0.62, 0.20, 0.18$	Uses $x = 1.6, k_4/k_3 = 0.89$
	$0.44, 0.26, 0.30$	Uses $x = 0.8, k_4/k_3 = 1.18$

<sup>a</sup> Preferred result.

and Thrush's  $7.9 \times 10^{15}$ . The pulse radiolysis value of Hikida, *et al.*,<sup>8</sup> is  $5.9 \pm 0.3 \times 10^{15}$ , which is also in agreement with our own within experimental error.

The distribution of the rates between the three possible paths  $k_2, k_3, k_4$  is given at the bottom of Table II. It is in rather poor agreement with the distribution 0.43, 0.05, 0.52 reported by Dodonov, *et al.*,<sup>19</sup> although their method seems considerably less direct than our own. The main disagreement is in the relative importance of  $k_3$  and  $k_4$ . We believe our distribution may be reasonable, however. The respective exothermicities of the three paths are 57, 38, and 55 kcal/mol. Since reactions 2 and 3 both involve the simple abstraction of H or O from either end of the H-O-O radical, it would be expected that  $k_2 > k_3$ , since the H-O bond in HO<sub>2</sub> is considerably weaker than the O-O bond. Reaction 4 is the slowest of the trio, which is also not surprising. Even though the exothermicity is about the same as reaction 2 it is a reaction where the colliding H must take the place of the end O atom in H-O-O, a relatively unlikely process. These conclusions about the relative importance of reactions 2, 3, and 4 are not significantly affected by the uncertainty in  $k_5$  noted earlier. The value assumed for  $k_6$  also affects the distribution, and the various possibilities are given in Table II. We prefer the combination  $k_6 = 1.9 \times 10^{13}$ ,  $k_5 = 1.5 \times 10^{12}$ .

We are now in a position to consider the results of adding CO to the H-O<sub>2</sub>-M reacting mixture. Unlike the case without CO, there is now no simple proportionality between (OH) and (H) to test the attainment

of a steady-state condition. The time required for attaining a steady state (HO<sub>2</sub>) is not lengthened by adding (CO), and under similar conditions this should still be very short (of the order of a millisecond, which is similar to the mixing time itself). Thus, let us assume first that *only* (HO<sub>2</sub>) is in steady state. As shown earlier, this leads to eq 10 for (HO<sub>2</sub>)<sub>s</sub> and the integral relation given as eq 11. Knowing all the rate constants (or ratios) which appear in this equation (from the results without CO, and elsewhere) a measurement of (H)/(O<sub>2</sub>) and (OH)/(O<sub>2</sub>) between two positions of the movable injector allows  $k_7/k_3$  to be determined by iteration. Let us call this method I.

Numerical values required in eq 11 were those derived from this work as given in Table II, in addition to  $k_5 = 1.5 \times 10^{12}$  as discussed earlier, and  $k_8 = 1.0 \times 10^{11}$  (the average of values from ref 9 and 10). Actually, the second term on the right side of eq 11 contributes very little, so that the precise value assumed for  $k_5$  is not very important. The integrals were evaluated numerically using various assumed values of  $k_7/k_3$ , the measurements (taken at 5-cm intervals) extending over a distance of 20 or 30 cm in the reactor ( $\approx 60$ –90 msec). The  $k_7/k_3$  values giving the best fit to the measured changes in H and OH on the left side of eq 11 are summarized in Table III as method I.

The second method of data analysis in the presence of CO is to assume both OH and O are in steady state

(19) A. F. Dodonov, G. K. Lavrovskaya, and V. L. Tal'roze, *Kinet. Katal.*, **10**, 701 (1969).

**Table III:** Summary of Results for  $k_7/k_8$ <sup>a,b</sup>

$P$ , Torr	$(O_2) \times 10^8$ , mol/cm <sup>3</sup>	$(CO) \times 10^8$ , mol/cm <sup>3</sup>	$(CO)/(H)$ (at $z = 0$ )	$(OH)/(H)$	$k_7/k_8$	
					Method I	Method II
2.08	2.54	0.92	19.2	0.025	0.045	Neg.
1.95	2.14	0.95	21.4	0.018	0.032	1.82
3.27	3.29	1.02	26.6	0.035	0.077	0.34
3.86	3.43	1.45	59.7	0.033	0.043	0.28
3.78	3.34	0.81	33.3	0.053	0.075	0.29
5.25	3.15	0.80	28.6	0.062	0.10	0.28
3.47	2.93	0.84	25.9	0.038	0.055	0.28
3.48	2.94	0.82	25.0	0.042	...	0.49
2.77	2.34	0.65	12.7	0.026	...	0.21
3.52	2.99	0.86	28.5	0.041	...	0.36

Av  $0.06 \pm 0.02$ 

<sup>a</sup> Method I:  $(HO_2)$  assumed in steady state, iteration in eq 11. Method II:  $(HO_2)$ ,  $(OH)$ , and  $(O)$  assumed in steady state, eq 12 and 13. <sup>b</sup> Constants used:  $k_1 = 6.8 \pm 1.0 \times 10^{15}$ ,  $k_w = 1.8 \times 10^8$ ,  $k/k_8 = 3.70$ ,  $k_4/k_3 = 0.39 \pm 0.06$ ,  $x = 1.6 \pm 0.3$ ,  $k_5 = 1.5 \times 10^{12}$ ,  $k_8 = 1.0 \times 10^{11}$ .

(in addition to  $HO_2$ ) and use eq 12 and 13. This is a simpler procedure of course, since the solution for  $k_7/k_8$  is in closed form. A summary of results with this method is given in the final column of Table III, using the same required constants as with method I and the measured  $(OH)$  and  $(H)$  at the  $z = 0$  position. The difference in the results by the two methods is apparent. Except for the first two runs which seem clearly anomalous, the  $k_7/k_8$  values by method II show somewhat less scatter than those by I and are consistently higher. In view of the additional assumptions involved in II, however, and the lack of a good way to check that  $(OH)$  and  $(O)$  really attain a steady-state condition as assumed, we are inclined to favor the results of method I. It seems most unlikely that the addition of CO to the  $H-O_2-M$  system, which was shown earlier to give the behavior expected of a steady-state  $(HO_2)$  condition, would cause this assumption to be invalidated, since all the CO does to  $HO_2$  is to add to its consumption rate. This could only tend to make the steady-state  $(HO_2)$  assumption more valid, and it is the only assumption involved in method I. On the other hand, it is conceivable that the addition of an appreciable OH generating reaction such as reaction 7 might upset the  $(OH)$  steady-state condition and invalidate method II. This point remains moot.

The value for  $k_7/k_8$  measured (about 0.06 by method I) seems somewhat unexpected at first sight, since it implies that reaction 7 must be moderately fast if reaction 3 is very fast, as is likely. For example, if  $k_3 \approx 10^{13}$  (the analogous reaction  $H + NO_2 \rightarrow NO + OH$  has a rate constant<sup>20</sup> of  $3 \times 10^{13}$ ), then we would have  $k_7 \approx 6 \times 10^{11}$ . The only previous estimate of  $k_7$  in the literature (based on anything more than conjecture) of which we are aware is that of Baldwin and coworkers<sup>21</sup> from the CO-sensitized decomposition of  $H_2O_2$  at  $440^\circ$ , who infer that the activation energy  $E_7$  is at least 23 kcal/mol. Based on their estimated pre-exponential factor of  $6 \times 10^{13}$  (which is "normal"),

this would give a completely negligible  $k_7$  at room temperature, which is at variance with the conclusion of the present work.

On closer examination it seems to us that there is no reason why  $k_7$  should not be reasonably large—comparable to  $k_3$ , or even larger. Reaction 7 is considerably more exothermic than reaction 8 (64 kcal/mol compared to 25). Both reactions represent the abstraction of an O atom by CO, and the O–O bond broken in  $HO_2$  is much weaker than the O–H bond in OH, as reflected by the difference in exothermicity. Thus on an energetic basis it might be expected that  $k_7 \geq k_8$ . Nor are there any spin conservation problems with reaction 7, which is analogous to reaction 8 in this respect. We conclude, therefore, that our result for  $k_7$  is reasonable and that a very high activation energy for this reaction would be surprising.

## Appendix

To communicate a feeling for the sensitivity of the derived  $k_7/k_8$  to the basic experimental measurements, the iteration for the first run in Table III will be outlined as a typical example. Over a 20-cm range in the reactor, the ratio  $(H)/(O_2)$  decreased from  $189 \times 10^{-4}$  to  $50 \times 10^{-4}$ , while  $(OH)/(O_2)$  decreased from  $4.8 \times 10^{-4}$  to  $1.8 \times 10^{-4}$ . Thus the left side of eq 11 had an experimental value  $\Delta = 142 \pm 19 \times 10^{-4}$ , where the assigned error limit represents the pessimistic estimated error<sup>13</sup> of about  $\pm 10\%$  in measuring the esr integrated intensities. The dominance of the  $(H)$  measurement in determining  $\Delta$  is apparent. We now use the rate constant values indicated above and iterate the right side of eq 11 with  $k_7/k_8$  (numerically integrating at 5-cm intervals corresponding to the measured decays of H and OH). Denote the first

(20) L. F. Phillips and H. I. Schiff, *J. Chem. Phys.*, **37**, 1233 (1962).

(21) R. R. Baldwin, R. W. Walker, and S. J. Webster, *Combust. Flame*, **15**, 167 (1970).

Table IV

$I_2$	Assumed $k_7/k_8$	$I_1$	$I_1 + I_2$
$4.5 \times 10^{-4}$	0	$192 \times 10^{-4}$	$196 \times 10^{-4}$
	0.01	176	180
	0.02	162	166
	0.03	152	156
	0.04	142	146
	0.05	133	137

term on the right side of eq 11 by  $I_1$  and the second by  $I_2$ , the value of  $k_7/k_8$  affecting only  $I_1$ . The iteration

in Table IV was then obtained. Interpolation between the last two iterations yields the  $k_7/k_8 = 0.045$  given in Table III. From the error estimated for  $\Delta$  one would infer an error of about  $\pm 0.02$  in  $k_7/k_8$ . The result is more sensitive to the value used for  $k/k_8$ . If a  $k/k_8$  larger than the 3.70 (a lower limit according to the possibilities of Table II) measured in the present work (with no CO) is used, the values of  $k_7/k_8$  derived from the data would be larger than those quoted in Table III. For example, use of  $k/k_8 = 5$  gives an iteration value  $k_7/k_8 = 0.08$  instead of 0.045 for the first run in Table III.

## Substituent Effects. IX. Correlation of Carbon-13, Proton-1, and Fluorine-19

### Nuclear Magnetic Resonance Chemical Shifts of Some Aromatic

### Compounds by Pairwise Additivity

by Edmund R. Malinowski

Department of Chemistry and Chemical Engineering, Stevens Institute of Technology, Hoboken, New Jersey 07030  
(Received January 6, 1972)

Publication costs borne completely by The Journal of Physical Chemistry

Carbon-13 shifts of heterocyclic nitrogen-containing aromatic compounds are found to be pairwise additive. Proton shifts of chloro- and hydroxy-substituted benzenes also obey pairwise additivity. Similarly, the fluorine shifts of chlorinated perfluorobenzenes are pairwise additive. The additivity scheme is expressed in terms of pairwise corrections to direct additivity. The pairwise corrections are believed to be the result of interactions between pairs of substituents within the molecule, in accord with the theoretical work of Vladimiroff and Malinowski.

### Introduction

Empirical correlations of nmr chemical shifts are extremely useful for assigning shifts and, hence, for deducing the structures of molecules. Such schemes are usually based upon the observation of shifts of a series of molecules which differ in structure in some systematic manner, such as the introduction of substituent groups into parent molecules. An ideal correlation involves a minimum number of empirical parameters while yielding a maximum degree of accuracy. Furthermore, empirical correlations provide valuable clues for deciphering the theoretical nature of nmr phenomena.

The pairwise additivity rule is a general scheme which has been shown<sup>1</sup> to be obeyed by a large variety of nuclei and a large variety of molecular systems. Spin-spin couplings as well as chemical shifts have been correlated

with the pairwise rule. For example, the shifts of carbon-13,<sup>2</sup> fluorine-19,<sup>1</sup> boron-11,<sup>1</sup> aluminum-27,<sup>3</sup> and proton-1<sup>1</sup> and couplings such as C-H,<sup>4-6</sup> C-F,<sup>7</sup> Si-H,<sup>7</sup> and Sn-H<sup>8</sup> follow pairwise additivity. Using McWeeny group functions, Vladimiroff and Malinowski<sup>1</sup> were able

(1) T. Vladimiroff and E. R. Malinowski, *J. Chem. Phys.*, **46**, 1830 (1967).

(2) E. R. Malinowski, T. Vladimiroff, and R. F. Tavares, *J. Phys. Chem.*, **70**, 2046 (1966).

(3) E. R. Malinowski, *J. Amer. Chem. Soc.*, **91**, 4701 (1969).

(4) E. R. Malinowski, L. Z. Pollara, and J. P. Larmann, *ibid.*, **84**, 2649 (1962).

(5) E. R. Malinowski, *ibid.*, **83**, 4479 (1961).

(6) A. W. Douglas, *J. Chem. Phys.*, **40**, 2413 (1964).

(7) T. Vladimiroff and E. R. Malinowski, *J. Amer. Chem. Soc.*, **86**, 3575 (1964).

(8) T. Vladimiroff and E. R. Malinowski, *J. Chem. Phys.*, **42**, 440 (1965).