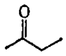
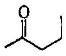
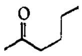
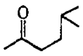
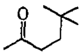
Table I. Comparison of Photochemical and Spectroscopic Calculations for Type II Photoreactions[a]

Molecule		ϕ_f^{rel}	τ_s^{rel}	τ_s, nsec	k_r^s(this work), sec^{-1}	k_r^s(Yang), sec^{-1}
	**(1)**	1.00	1.00	2.5		
	**(2)**	0.82	0.72	1.8	1.5×10^8	1.8×10^8
	**(3)**	0.39	0.32	0.81	8.4×10^8	9.9×10^8
	**(4)**	0.17	0.14	0.35	2.5×10^9	2.1×10^9
	**(5)**	1.02				

[a] Relative quantum yields of fluorescence for the ketones were obtained in *n*-hexane solution (~0.1 *M*) using an Aminco-Bowman spectrofluorometer. Correction was made for small differences in absorbance at the excitation wavelength, 313 nm.

methyls (**5**), the relative fluorescence quantum yield undergoes a large increase to a value near unity. This implies that intramolecular abstraction of δ hydrogens does not compete favorably with intersystem crossing in the S_1 state of **5**. Irradiation of **5** has been reported to result only in intermolecular photoreduction.[4]

Although the position and shape of the uv absorption bands of ketones **1**-**5** are all very similar, ϵ_{max} does increase with increasing methyl substitution. An increase in ϵ_{max} would result in a larger value of k_f (eq 3) and thus a higher quantum yield of fluorescence (eq 2). In order to normalize for this effect, we have used eq 4 to obtain the relative singlet lifetimes (τ_s^{rel})

$$\tau_s^{rel} = \phi_f^{rel}/\epsilon_{max} \qquad (4)$$

reported in the table. The absolute singlet lifetimes (τ_s) were calculated from the τ_s^{rel} values and the singlet lifetime of 2-pentanone, which we have measured by single-photon counting[5] to be 1.8×10^{-9} sec. Since for alkyl ketones $k_{st} \gg k_f$, and Yang[3] has shown that k_{st} for this series is insensitive to substitution at the γ carbon, we can attribute the decrease in τ_s as we go from **1** to **4** to some special interaction of the n,π^* excited singlet state with the γ-C-H bond. Thus, the k_r^s(this work) values given in the table are the increase in the S_1 decay rate ($1/\tau_s$) relative to 2-butanone (**1**). Since these k_r^s values do not distinguish a chemically productive interaction of the n,π^* S_1 state with the γ hydrogen from a physical, nonchemically productive interaction, they should be compared to the sum (k_r^s(Yang)) of Yang's rate constants[3] for type II and nonradiative decay from the first excited singlet state. If all the nonradiative decay results from reversion of an initially formed 1,4 biradical to the starting ketone, then k_r^s represents the reactivity toward the initial γ-hydrogen abstraction from S_1.

The agreement between the k_r^s values determined in this work and those determined by Yang and coworkers[3] by chemical-quenching techniques is excellent and clearly demonstrates the applicability and value of using the fluorescence characteristics of compounds to extract information on the reactivity of excited singlet states toward primary photochemical processes. The data also indicate that eq 3 is valid to a reasonable degree of precision for calculating relative k_f values. Attempts to use such a formula to calculate absolute k_f values appears to be accurate only for order of magnitude estimates.[6]

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(4) N. C. Yang, "Reactivity of the Photoexcited Organic Molecule," Wiley, New York, N. Y., 1967, p 149.

(5) F. S. Wettack, G. D. Renkes, M. C. Rockley, N. J. Turro, and J. C. Dalton, *J. Amer. Chem. Soc.*, **92**, 1793 (1970).

(6) M. O. Sullivan and A. Testa, *ibid.*, **92**, 5842 (1970); R. F. Borkman and D. R. Kearns, *ibid.*, **88**, 3467 (1966); *J. Chem. Phys.*, **44**, 945 (1966).

Mass Spectrometric Study of the Reactions of the Hydroxyl Radical with Ethylene, Propylene, and Acetaldehyde in a Discharge-Flow System

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Abstract: The reaction of hydroxyl (OH) radicals with ethylene (C_2H_4), propylene (CH_3CHCH_2), and acetaldehyde (CH_3CHO) has been studied mass spectrometrically in a discharge-flow system at 300°K. Bimolecular rate constants for these reactions are: $k_{OH+C_2H_4} = 1.8 \times 10^{-12}$, $k_{OH+CH_3CHCH_2} = 1.7 \times 10^{-11}$, and $k_{OH+CH_3CHO} = 1.5 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}. These OH radical reactions are much faster than the corresponding O atom reactions and should play an important role in photochemical smog and in combustion. In OH + C_2H_4 and OH + CH_3CHCH_2, the OH adducts have been observed directly. The overall reaction mechanisms are discussed briefly on the basis of qualitative product analysis.

Reactions of OH radicals with olefins and with aldehydes are of current interest because of their role in combustion[1] and in photochemical smog. In particular, reactions of OH with unsaturated compounds have been proposed as an important chain-propagating step in photochemical oxidations.[2,3] However, the

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(1) W. E. Wilson, "A Critical Review of the Gas Phase Reaction Kinetics of Several Bimolecular Reactions of the Hydroxyl Radical," NSRDS-NBS, in press.

(2) D. H. Stedman, E. D. Morris, Jr., E. E. Daby, H. Niki, and B. Weinstock, 160th National Meeting of the American Chemical Society, Chicago, Ill., 1970, Abstract No. WATR 26.

kinetics and mechanisms of these reactions are not well established. Previously, the reaction of OH with ethylene (C_2H_4) was studied by Wilson and Westenberg[4] in a flow-discharge system using esr, and by Greiner[5] in flash photolysis using uv absorption spectroscopy. These authors measured the exponential decay of OH in the presence of a large excess of C_2H_4 and analyzed the kinetic behavior of OH by the general equation

$$\ln [(\mathrm{OH})_{t_1}/(\mathrm{OH})_{t_2}] = nk(\mathrm{C_2H_4})(t_2 - t_1) \qquad (1)$$

where k is the bimolecular rate constant for $OH + C_2H_4$ and n is the stoichiometric number; *i.e.*, the number of OH consumed per C_2H_4 reacted. According to eq (1) the value of n must be determined to derive the rate constant, because it is difficult to avoid fast secondary reactions of OH with product radicals. The preliminary results of Wilson and Westenberg give an apparent rate constant, nk, of 5×10^{-12} cm^3/(molecule sec). Greiner has obtained the same value for k by applying an estimated stoichiometric correction to his data.

Avramenko and Kolesnikova[6] have measured rate constants for a number of OH reactions, including those with ethylene and acetaldehyde. However, their values are generally several orders of magnitude too small. The water-discharge method which they used to generate OH has been shown to be unsuitable for kinetic studies.[1,7] No study has been reported for the reaction of OH with propylene (CH_3CHCH_2).

In the present study, a mass spectrometer was used to monitor both OH and hydrocarbon reactants (RH). Rate constants were determined using eq 1 by measuring both the exponential decay of OH and the amount of RH consumed to give the stoichiometry. In addition, rate constants were determined directly from the decay of RH in the presence of an excess of OH as in

$$\ln [(\mathrm{RH})_{t_1}/(\mathrm{RH})_{t_2}] = k\int_{t_1}^{t_2}(\mathrm{OH})\mathrm{d}t \qquad (2)$$

In eq 2 the stoichiometry is taken to be unity. That is, RH reacts predominently with OH under OH-rich conditions. This is a valid assumption since reactive products will be preferentially consumed by the excess OH present. Furthermore, this study has shown that possible intermediate species such as O, H, and hydrocarbon radicals react with the RH at slower rates than OH. The use of a mass spectrometer has the additional advantage of allowing one to observe the reaction products.

Experimental Section

The flow-discharge apparatus coupled to a time-of-flight mass spectrometer has been described previously.[8] The flow of helium carrier gas was adjusted to give a flow velocity in the reactor of 30 m/sec at 1 Torr of pressure. A measured flow of H_2 was mixed with the helium and passed through a microwave discharge to produce H atoms. The H atoms were calibrated by the amount of H_2 consumed when the discharge was turned on. The walls of the reactor were treated with phosphoric acid.

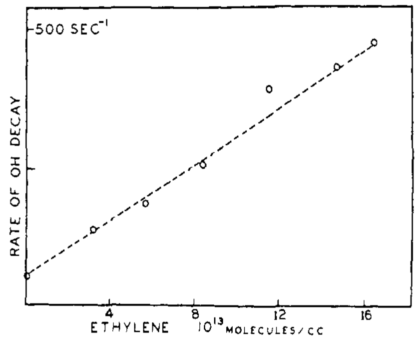

Figure 1. Plot of the OH decay as a function of ethylene concentration, showing nonzero intercept.

Hydroxyl radicals were produced by titrating H atoms with NO_2 according to the reaction $H + NO_2 \rightarrow OH + NO$. During a kinetic run enough excess NO_2 was added to consume all the H at the first measurement point. Several experiments under H atom excess conditions gave the same kinetic results. OH was detected directly by mass spectrometry at m/e 17 after suitable correction for the cracking pattern of water. The electron energy was kept low (20 eV) to minimize this interference. The initial OH concentration was determined from the H atoms or NO_2 consumed. At the low concentrations of OH used here (4×10^{12} molecules/cm^3) the decay along the reactor length (10 cm) was small (20%), requiring only a short extrapolation to the initial OH concentration. The decay appeared to be first order since the rate was the same at 2 and 4×10^{12} molecules/cm^3. If one takes the rate constants from Breen and Glass[9,10] for the decay of OH, and assumes the reaction $O + OH \rightarrow O_2 + H$ goes to completion, the calculated ratio of rates for the reactions $OH + OH \rightarrow H_2O + O$ and $OH \rightarrow$ wall shows that OH decay should be predominately first order at these concentrations. Because of the small extent of the second-order decay of OH, the subsequent reactions $O + OH \rightarrow O_2 + H$ and $H + NO_2 \rightarrow OH + NO$ did not cause the ratio of H consumed to NO_2 consumed to differ substantially from unity.

An additional check on the OH calibration was made by adding CO and converting a portion of the OH back to H by the reaction $OH + CO \rightarrow CO_2 + H$. This gives the relative sensitivities for H and OH, where H was calibrated previously. The three methods of OH calibration give consistent results to within 10%.

A pressure drop of 8% was observed over the portion of the reactor used for measurement. This is in good agreement with that calculated from Poiseuille flow. The rate constants were calculated assuming that the flow velocity and pressure were constant and equal to those in the middle of the reaction zone. All measurements were carried out at 300°K.

Rate constants for the reactions of OH with C_2H_4, CH_3CHCH_2, and CH_3CHO were determined by measuring the decay rates of OH as a function of RH concentration according to eq 1. However, correction must be made for the decay of OH with no RH added. Since this decay has been shown to be first order, it can be applied as a correction factor. The actual equation used was

$$\ln [(\mathrm{OH})_{t_1}/(\mathrm{OH})_{t_2}] = [nk(\overline{\mathrm{RH}}) + k_{\mathrm{wall}}](t_2 - t_1) \qquad (1a)$$

where k_{wall} includes some bimolecular decay approximated by a first-order constant. Alternately, the uncorrected rates can be plotted against RH as in Figure 1 to give a nonzero intercept and a slope corresponding to nk. The initial OH concentration was 2-5 $\times 10^{12}$ molecules/cm^3. The C_2H_4 concentration was varied over the range of 3–15 $\times 10^{13}$ molecules/cm^3, while CH_3CHCH_2 and CH_3CHO were varied from 2 to 5 $\times 10^{12}$ molecules/cm^3. In the case of CH_3CHCH_2 and CH_3CHO, measurable amounts of RH were consumed, allowing the ratio $\Delta OH/\Delta RH = n$ to be determined. This stoichiometry was then used to correct the apparent rate constant nk. In general, RH was added through the movable slider with the NO_2. Several experiments, performed by adding NO_2 upstream through a fixed inlet and RH through the slider, gave the same kinetic results. However, the OH wall decay correction was complicated by the changing surface area of the slider.

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(3) H. S. Johnston, Project Clean Air Task Force Assessments, University of California, 1970.

(4) W. E. Wilson and A. A. Westenberg, Proceedings of the 11th Symposium on Combustion, 1967, p 1143.

(5) N. R. Greiner, *J. Chem. Phys.*, **53**, 1284 (1970).

(6) L. I. Avramenko and R. V. Kolesnikova, *Advan. Photochem.*, **2**, 25 (1964).

(7) F. P. Del Greco and F. Kaufman, *Discuss. Faraday Soc.*, **33**, 128 (1962).

(8) H. Niki, E. E. Daby, and B. Weinstock, Proceedings of the 12th Symposium on Combustion, 1969, p 277.

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

(10) Literature values for the reaction $OH + OH$ range from 0.8 to 2.6×10^{-12} cm^3/(molecule sec); see ref 1 or 9.

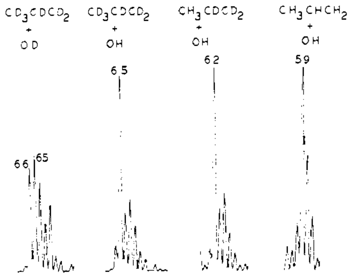

Figure 2. Adduct peaks observed in the reaction of OH with propylene.

As an alternative method, one would like to measure rate constants by eq 2 with a large constant concentration of OH. However, at OH concentrations of 1-2 × 10^{13} molecules/cm^3, the bimolecular decay becomes important and more than half the OH is lost over the length of the reactor. In practice the OH and RH concentrations are determined at several positions along the reactor. An integrated value of OH is determined for each interval and combined with the RH decay over that interval to give a rate constant. The hydrocarbon concentrations were maintained at a low level, typically 5 × 10^{11} molecules/cm^3. Rate constants obtained by this method were not affected by a twofold change in initial concentration of OH or RH.

Products

Product analysis could be made only qualitatively, since the intermediate products react rapidly with OH. In the reactions of OH with C_2H_4 and CH_3CHCH_2, mass peaks corresponding to OH adducts were observed. This observation was further confirmed in the reactions of OH and OD with C_2D_4, CH_3CDCD_2, and CD_3CDCD_2. Figure 2 shows the mass spectra observed with several propylene isotopes under conditions optimized for the adduct peaks. The OD experiment was contaminated with OH and shows peaks corresponding to both the OD and OH adducts. The adduct peaks were found to be enhanced as the total pressure was increased from 1 to 4 Torr. These results suggest that OH adds to C_2H_4 and CH_3CHCH_2 and that the adducts are collisionally stabilized.

Acetaldehyde is a major product in OH + C_2H_4. Propionaldehyde was observed in the reaction of OH + CH_3CHCH_2. In the reaction of OH with C_2D_4, CH_3CDCD_2, and CD_3CDCD_2, the H from OH is retained in the aldehyde while a deuterium from olefin is lost, presumably by abstraction by OH. A number of minor products are also seen, resulting from the further reaction of OH with the aldehydes. Products of OH + CH_3CHO include CH_3, CO, CO_2, and CH_2CO, with minor amounts of CH_3COOH and CH_3NO_2 (in excess NO_2). Avery and Cvetanović[11] have suggested that the primary reaction is abstraction of the aldehydic hydrogen. These products can then be accounted for by the subsequent reactions of CH_3CO with OH.

Discussion

Rate constants obtained by the two methods are summarized in Table I together with the stoichiometries observed in the CH_3CHCH_2 and CH_3CHO reactions. The rate constant for OH + C_2H_4 found in this study is a factor of 3 smaller than the values found by the two previous investigators. However, the present value is not in serious conflict with the results of Wilson and Westenberg since they measured only an apparent rate constant (*nk*) using a higher OH concentration. On the other hand, Greiner corrected his rate constant by estimating the stoichiometry based on a single secondary reaction. Under his experimental conditions and assuming a very fast secondary reaction, this correction is only about 10%. However, a serious source of error exists if OH reacts rapidly with the photolysis products of C_2H_4. The photolysis of ethylene is unavoidable since it absorbs strongly in the same spectral region as water, which is used as a source of OH. The present study is in agreement with that of Greiner that the initial step in the OH + C_2H_4 reaction is addition. However, the rate constant for this reaction should not be taken as typical of olefins in general as it is a factor of 10 smaller than that of CH_3CHCH_2. This striking variation in the reactivity of C_2H_4 and CH_3CHCH_2 reveals the electrophilic nature of OH in addition reactions.

Table I. Rate Constants for OH + C_2H_4, CH_3CHCH_2, and CH_3CHO[a]

	C_2H_4	CH_3CHCH_2	CH_3CHO
		From Eq 1	
nk	2.5×10^{-12}	5×10^{-11}	3×10^{-11}
n		3.2	1.9
k		1.6×10^{-11}	1.6×10^{-11}
		From Eq 2	
k	1.8×10^{-12}	1.8×10^{-11}	1.5×10^{-11}

[a] Rate constants are given in the units of cubic centimeters per molecule per second. Estimated overall uncertainty ±25%.

The rate constant found in this study for the reaction of OH with CH_3CHO is more than two orders of magnitude larger than that measured by Avramenko and Kolesnikova. This suggests that OH–aldehyde reactions may also be important in combustion and photochemical processes. It should also be noted that the reactions of OH with the olefins and aldehyde studied are much faster than the corresponding O atom reactions.[8,11,12]

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(11) H. E. Avery and R. J. Cvetanović, *J. Chem. Phys.*, 43, 3727 (1965).

(12) See, for example, R. J. Cvetanović, *ibid.*, 33, 1063 (1960).