# Kinetics of the Reactions of the Formyl Radical with Oxygen, Nitrogen Dioxide, Chlorine, and Bromine

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The gas-phase kinetics of the reactions of HCO with four molecules (O<sub>2</sub>, NO<sub>2</sub>, Cl<sub>2</sub>, and Br<sub>2</sub>) have been studied as a function of temperature in a tubular reactor coupled to a photoionization mass spectrometer. Rate constants for each reaction were determined at a minimum of five temperatures to obtain Arrhenius parameters ( $k = A \exp(-E_a/RT)$ ). The results obtained are as follows (the numbers in the brackets are log  $A/(\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$ ,  $E_a/(\text{kJ mol}^{-1})$ , and the temperature ranges covered): HCO + O<sub>2</sub> {-10.9 (±0.3), 1.7 (±1.5), 295-713 K}; HCO + NO<sub>2</sub> {-10.6 (±0.3), -1.8 (±2.0), 294-713 K}; HCO + Cl<sub>2</sub> {-11.2 (±0.3), 0.3 (±2.0), 296-582 K}; HCO + Br<sub>2</sub> {-10.8 (±0.3), -3.7 (±2.0), 296-669 K}. The reactivity of HCO was found to be between that of CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub> in the reactions of these radicals with Cl<sub>2</sub> and Br<sub>2</sub>, which is consistent with proposed correlations of reactivity in exothermic reactions based on free-radical ionization potentials.

## Introduction

The formyl radical is one of the important oxygen-containing intermediates formed during the oxidation of hydrogen-containing organic compounds. Knowledge of its kinetics is needed for the quantitative modeling of many gas-phase oxidation processes including tropospheric smog cycles<sup>1,2</sup> and the combustion of fossil fuels at elevated temperatures.<sup>3,4</sup> Information regarding its reactivity is, however, sparse because of the difficulty in isolating reactions of this labile intermediate for quantitative study as well as the relatively low reactivity of HCO except in reactions with other free radicals.

Particular attention has been focused on the kinetics of two rapid reactions involving the formyl radical because of their importance in atmospheric chemistry:

$$HCO + NO \rightarrow HNO + CO$$
 (ref 5-7) (1)

$$HCO + O_2 \rightarrow HO_2 + CO \quad (ref 5-10) \tag{2}$$

Rate constants have been measured, and evidence has been reported which indicates that their mechanisms involve association without an energy barrier followed by rapid isomerization and decomposition to produce the final products. Although the lifetimes of the energy-rich adducts formed appear to be too short to be stabilized in the gas phase at atmospheric pressure,<sup>11</sup> one of them, HCO<sub>3</sub>, has been produced and isolated for spectroscopic studies on a cold matrix.<sup>12,13</sup>

Other association reactions involving HCO with free radicals which have also been studied but to a lesser extent include HCO + HCO,<sup>14</sup> HCO + H,<sup>15</sup> HCO + O,<sup>16</sup> and HCO + OH.<sup>17</sup>

Recently the kinetics and mechanisms of several gas-phase reactions of HCO with olefins have also been investigated both experimentally and theoretically.<sup>18,19</sup> These studies were conducted, in part, to gain an indication of the reactivity of HCO in reactions other than those which involve recombination with other free radicals. The results obtained indicate that these R + olefin reactions proceed via an addition pathway. The measured rate constants reveal among other things that the reactivity of HCO (at least among these addition reactions) is somewhat greater than that of CH<sub>3</sub> but below that of NH<sub>2</sub>.<sup>19</sup>

To continue to develop an understanding of the reactivity of HCO, we have studied four reactions of this radical. Two are reactions between free radicals, reaction 2, and

$$ICO + NO_2 \rightarrow products$$
 (3)

and two reactions of HCO with closed-shell molecules

 $HCO + Cl_2 \rightarrow HCOCl + Cl, \Delta H = -81 \text{ kJ mol}^{-1}$  (4)

HCO + Br<sub>2</sub> 
$$\rightarrow$$
 HCOBr + Br,  $\Delta H = -68 \text{ kJ mol}^{-1}$  (5)

The products of reactions 2, 4, and 5 have already been established. The yield of HO<sub>2</sub> from reaction 2 has been measured by Temps and Wagner and found to be  $1.0 \pm 0.07$ .<sup>10</sup> Niki and co-workers have produced the halogenated formaldehydes, HCOCl and HCOBr, for spectroscopic studies using reactions 4 and 5.<sup>20,21</sup> It was concluded in these investigations that these reactions proceed essentially exclusively as indicated since no other products of either the HCO + Cl<sub>2</sub> or HCO + Br<sub>2</sub> reaction were observed.<sup>20,22</sup>

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Figure 1. Plot of first-order decay constants (k') vs  $[O_2]$  for a series of experiments conducted at 531 K. Insert is the HCO<sup>+</sup> ion signal profile recorded during the experiment when  $[O_2] = 7.6 \times 10^{12}$  molecules cm<sup>-3</sup> The line through the ion signal profile is an exponential function fitted by a nonlinear least-squares procedure  $(k' = 96.6 \text{ s}^{-1})$ .

Reactions 2-5 were studied in a heatable tubular reactor coupled to a photoionization mass spectrometer. Rate constants were measured as a function of temperature to obtain the Arrhenius parameters of reactions 2-5. There have been no prior determinations of  $k_3 - k_5$  at any temperature. A description of these experiments and the results obtained are reported here together with a discussion of the reactivity of the HCO radical.

#### **Experimental Section**

The experimental apparatus used and procedures employed to reduce the data have been described previously.<sup>23,24</sup> Pulsed 308-nm radiation (5 Hz) from a Lambda Physik EMG 101E excimer laser was directed along the axis of a heatable 1.05 cm i.d., coated (with boric acid) tubular quartz reactor. Gas flowing through the tube at 5 m s<sup>-1</sup> was completely replaced between laser pulses. The flowing gas contained CH<sub>3</sub>CHO (the HCO source; typically 0.05%), the second reactant gas (0-0.35%), and the carrier gas (He) which was always in great excess (>99%). Gas was sampled through a 0.08 cm diameter hole (located at the end of a nozzle in the wall of the reactor) and formed into a beam by a conical skimmer before it entered the vacuum chamber containing the photoionization mass spectrometer. As the gas beam traversed the ion source, a portion was photoionized and then mass selected. Temporal ion signal profiles were recorded from a short time before each laser pulse to 10-28 ms following the pulse using a multichannel scalar. Typically data from 5000 to 30 000 repetitions of the experiment were accumulated before the data were analyzed.

Reactions 2-5 were studied under pseudo-first-order conditions with the stable reactant in large excess. Formyl radical decay profiles were exponential in shape under all experimental conditions as expected. They were fit to an exponential function  $([HCO]_t = [HCO]_0 \exp(-k't))$  using a nonlinear least-squares procedure (see insert in Figure 1). The decay constant k' was measured as a function of the concentration of the second reactant to obtain the rate constant of the reaction under study.

Initial HCO concentrations from the photodissociation of CH<sub>3</sub>CHO were kept sufficiently low ( $< 5 \times 10^{10}$  molecule cm<sup>-3</sup>) to assure that reactions between the free radicals produced by the photolysis of CH<sub>3</sub>CHO had negligible rates compared to the reaction under study. This condition was verified under each set of experimental conditions from observations of the independence of k' on laser intensity and  $CH_3CHO$  concentration (both of which, when changed, alter the initial free-radical concentrations).

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Under the conditions described above, HCO is produced instantly by the photolysis process

$$CH_3CHO \xrightarrow{300 \text{ nm}} CH_3 + HCO$$
 (ref 25, 26) (6)

and is subsequently lost in only two reactions:

$$HCO + A \rightarrow products$$
 (A)

$$HCO \rightarrow heterogeneous loss$$
 (B)

(A is  $O_2$ ,  $NO_2$ ,  $Cl_2$ , or  $Br_2$ .) The rate constants for reaction A under each set of experimental conditions were obtained from slopes of plots of k'vs [A] since, for the above mechanism, k' = $k_{\rm A}[{\rm A}] + k_{\rm B}$  (See Figure 1).

The 308-nm photolysis of CH<sub>3</sub>CHO resulted in such a small degree of decomposition during each pulse that only an upper limit (0.3%) could be established for the extent of this process. For this reason only an upper limit could be determined for the initial HCO (and CH<sub>3</sub>) concentrations,  $5 \times 10^{10}$  molecules cm<sup>-3</sup>.

The 308-nm laser radiation also photodecomposed the stable molecular reactants to a limited extent: NO<sub>2</sub> (<2%), Cl<sub>2</sub> (<2.4%), and  $Br_2$  (<0.1%). The atoms produced (O, Cl, or Br) reacted rapidly with CH<sub>3</sub>CHO producing acetyl radicals (and perhaps formylmethyl radicals (CH<sub>2</sub>CHO)):

## $(O, Cl, Br) + CH_3CHO \rightarrow (OH, HCl, HBr) + CH_3CO$ (7)

The photoproduction of these atoms and their subsequent conversion to acetyl radicals by reaction 7 did not interfere with the study of the reaction of interest because formyl radicals were not regenerated by reaction 7. In addition, the concentrations of the additional free radicals produced by these secondary processes were generally still too low to cause interference from radical-radical reactions (e.g.,  $HCO + CH_3CO$ ).

To determine whether the photolysis of the stable molecular reactants resulted in the production of excessive concentrations of additional free radicals, two kinds of tests were performed. First, in each set of experiments in which the HCO decay constant was measured as a function of [A], the decay constant was measured at one of these concentrations by using two different laser fluences which were a factor of 2 apart. These tests compared decay constants from experiments in which the total concentrations of free radicals from all sources were a factor of 2 apart. In no case was the HCO decay constant altered by this change in fluence by a measurable extent (<5%). These results indicate that radical-radical processes involving HCO still had negligible rates in the presence of the additional free radicals produced by reaction 7. This conclusion was anticipated based on calculated maximum CH<sub>3</sub>CO concentrations using the measured upper limits of photodecomposition of  $NO_2$  and  $Br_2$ . However, in the case of  $Cl_2$ , calculated maximum CH<sub>3</sub>CO concentrations were sufficiently high that interference by recombination processes involving HCO was anticipated.

A second test was performed to further assess the possible interference of radical-radical reactions in the study of the HCO +  $Cl_2$  reaction. During that part of the study of reaction 4 which was conducted at 399 K, decay profiles of CH<sub>3</sub> (produced by the same photolysis of CH<sub>3</sub>CHO (reaction 6)) were recorded along with those of HCO. These additional data were used to obtain a rate constant for the  $CH_3 + Cl_2$  reaction. The measured value  $(2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1})$  is within 5% of the value for the

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 $CH_3 + Cl_2$  rate constant measured at this temperature in a prior investigation in our laboratory:<sup>24</sup> In this earlier study, the photolysis of  $Cl_2$  was considerably less important (<0.8%), and no interference by radical-radical reactions was expected or detected. The fact that the measurement of the  $CH_3 + Cl_2$  rate constant was not affected by the presence of secondary free radicals is a strong indication that the measurements of the HCO +  $Cl_2$  rate constant (in exactly the same system) were similarly unaffected.

The results of the two different tests described above provide the necessary evidence to conclude that radical-radical reactions involving HCO had negligible rates in these experiments and therefore did not interfere with the isolation and study of reactions 2-5. The fact that the anticipated interference from the HCO + CH<sub>3</sub>CO recombination process was not observed in the study of the HCO + Cl<sub>2</sub> reaction is probably due to the fact that this recombination reaction actually has a significantly lower rate constant than was presumed in our assessment. We used an estimated high-pressure limiting value for the HCO + CH<sub>3</sub>CO recombination rate constant ( $5 \times 10^{-11}$  cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>). This reaction is probably significantly into the falloff region at the pressures used in our studies (0.5-2 Torr), and the actual bimolecular recombination rate constant for this pressure range is probably below the presumed value.

Searches for reaction products were inconclusive except for the detection of  $HO_2$  as a product of reaction 2. There were two basic reasons for the inability to detect or to establish other products. In some instances, detected possible products could not be unequivocally associated with the reaction under study because other free radicals in the system were capable of producing the same product. For example, NO production was observed during the HCO + NO<sub>2</sub> reaction. However, since the  $CH_3 + NO_2$  reaction also produces NO at essentially the same rate expected by reaction 3, the observed appearance of nitric oxide was not evidence that NO was also produced by reaction 3. The halogenated formaldehyde molecules, HCOCl and HCOBr, were not detected in the studies of reactions 4 and 5. This was probably due to inadequate detection sensitivity. The combination of the very low initial HCO concentrations used in this study and the lower inherent sensitivity of the photoionization mass spectrometer when ionization is done with the argon resonance lamp (11.6 eV) combined to make these products difficult to detect. The  $HO_2$ produced by reaction 2 was barely detectable by using this same photoionization energy.

The photoionization energies (in eV) used to detect or attempt to detect reactants and products were 11.6-11.8 (Cl<sub>2</sub>, Br<sub>2</sub>, HO<sub>2</sub>, HCOCl, and HCOBr) and 10.2 (CH<sub>3</sub>CHO, NO<sub>2</sub>, NO, and HCO).

The sources of the materials used were Mallinckrodt (CH<sub>3</sub>CHO, min 99%), Matheson (Cl<sub>2</sub>, min 99.5%; NO<sub>2</sub>, min 99.5%; O<sub>2</sub>, 99.99%), Linde (He, 99.995%), and J. T. Baker (Br<sub>2</sub>, min 98%). The compounds CH<sub>3</sub>CHO and Cl<sub>2</sub> were degassed by freeze-pump-thaw cycles and used without further purification. NO<sub>2</sub> was repeatedly fractionally distilled (6-8 times) to remove all NO, and Br<sub>2</sub> was fractionally distilled twice before use. Helium was used as provided.

The conditions and results of experiments performed to measure the rate constants of reactions 2-5 are presented in Table I. The most probable uncertainty in each measured rate constant is  $\pm 20\%$ . The Arrhenius parameters for  $k_2-k_5$  are included in Table I. The error limits for these parameters again are the most probable uncertainties and reflect the temperature ranges covered in each study as well as the uncertainties in each measured rate constant. The measured rate constants are plotted in Figure 2 together with the corresponding Arrhenius rate constant functions.

#### Discussion

1. Comparison with Other Studies. Of the four reactions studied only the HCO +  $O_2$  reaction has been the subject of prior investigations.<sup>5-10</sup> There have been several determinations of  $k_2$  at room temperature, but in only one of these earlier studies was its temperature dependence studied.<sup>7</sup> Our "room temperature" value of  $k_2$  (6.2 × 10<sup>-12</sup> at 295 K) is in good agreement with other

TABLE I: Conditions and Results of Experiments To Measure Rate Constants of the Reactions of Formyl Radicals with  $O_2$ ,  $NO_2$ ,  $Cl_2$ , and  $Br_2^a$ 

• 4												
	Р,	$10^{-12}[X],$	$10^{12}k^{c}$ cm <sup>3</sup>									
<i>T</i> , <sup><i>b</i></sup> K	Torr	molecules cm <sup>-3</sup>	$k_{\rm B},  {\rm s}^{-1}$	molecule <sup>-1</sup> s <sup>-1</sup>								
$HCO + O_2 \rightarrow CO + HO_2 (X = O_2)$												
$(\log A_2 = -10.9 \pm 0.3; {}^d E_2 = 1.7 \pm 1.5^d)$												
295	0.52	7.6-55.6	. 34	6.2								
	$(1.03)^{e}$	(17.8 - 40.9)										
349	0.91	6.1-42.2	26	6.6								
422	0.88	6.9-49.3	33	7.2								
531	0.91	7.6-50.4	39	7.4								
610	0.92	6.7-37.4	62	8.2								
713	0.92	6.6-29.8	105	10								
	(1.51)	(7.5-28.5)	(132)	9.6								
HCO + NO <sub>2</sub> $\rightarrow$ products (X = NO <sub>2</sub> )												
$(\log A_3 = -10.6 \pm 0.3; {}^d E_3 = -1.8 \pm 2.0^d)$												
294	0.51	2.13-6.27	29	56								
342	0.50	1.73-4.69	36	43								
399	0.48	2.14-6.44	48	54								
479	0.90	2.29-6.98	33	44								
582	1.10	1.75-7.74	47	37								
713	0.87	1.52-6.98	100	35								
$HCO + Cl_2 \rightarrow HCOCl + Cl (X = Cl_2)$												
$(\log A_4 = -11.2 \pm 0.3; ^d E_4 = 0.3 \pm 2.0^d)$												
296	0.56	2.0-75.2	61	7.1								
295	1.45	4.3-21.4	101	7.3								
342	1.21	4.6-46.8	93	8.6								
399	0.45	5.2-35.1	83	8.9								
479	0.76	4.2-52.0	80	6.6								
582	1.25	9.2-46.6	98	7.4								
$HCO + Br_2 \rightarrow HCOBr + Br (X = Br_2)$												
$(\log A_5 = -10.8 \pm 0.3; {}^d E_5 = -3.7 \pm 2.0^{\tilde{d}})$												
296	1.06	1.43-5.36	62	72								
343	1.23	1.59-4.57	64	59								
410	1.49	1.47-6.31	54	62								
508	1.85	1.41-8.89	61	36								
669	2.46	2.09-11.4	126	32								

<sup>a</sup> [CH<sub>3</sub>CHO] =  $(0.9-1.6) \times 10^{13}$  molecules cm<sup>-3</sup> (typically 1.2 × 10<sup>13</sup>); [HCO]<sub>0</sub> =  $<5 \times 10^{10}$  molecules cm<sup>-3</sup> in all experiments (based on a measured upper limit of 0.3% decomposition of CH<sub>3</sub>CHO). <sup>b</sup> Temperature uncertainty ±3 K (295-400 K), ±4 K (401-500 K), ±5 K (501-600 K), ±6 K (>600 K). <sup>c</sup> Most probable uncertainty estimate in each rate constant ±20%. <sup>d</sup> Units of A are cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>. Units of E<sub>a</sub> are kJ mol<sup>-1</sup>. Error limits are most probable uncertainties. <sup>e</sup> Numbers in parentheses indicate other conditions used in the rate constant determination at this temperature.



Figure 2. Semilog plot of measured bimolecular rate constants of HCO reactions with  $Br_2$ ,  $NO_2$ ,  $Cl_2$ , and  $Br_2$ . The lines fitted through the plotted points by linear least squares were used to obtain the Arrhenius parameters of each rate constant (given in Table I). Vertical bars on open symbols are the estimated most probable errors of the measured rate constants. Those on the closed circles are the error limits presented in the study of the HCO +  $O_2$  reaction by Veyret and Lesclaux.<sup>7</sup>

TABLE II: Rate Constants of R + Cl<sub>2</sub> and R + Br<sub>2</sub> Reactions

	IP, <sup>c</sup> eV	$\mathbf{R} + \mathbf{Cl}_2^a$			$R + Br_2^b$			
R		$\log A$ , cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	E <sub>a</sub> , kJ mol <sup>-1</sup>	$k(298), cm^3$ molecule <sup>-1</sup> s <sup>-1</sup>	$\log A$ , cm <sup>3</sup> molecule <sup>-1</sup> s <sup>-1</sup>	$E_{a},$ kJ mol <sup>-1</sup>	$k(298), \text{ cm}^3$ molecule <sup>-1</sup> s <sup>-1</sup>	
CH <sub>3</sub>	9.8	-11.3	2	$2.1 \ (-12)^d$	-10.8	-2	4.2 (-11)	
HCO	8.6	-11.2	0	7.1 (-12)	-10.8	-4	7.5 (-11)	
$C_2H_5$	8.4	-10.9	-1	1.8 (-11)	-10.5	-3	1.1 (-10)	
<i>i</i> -Ĉ₃Ĥ <sub>7</sub>	7.4	-10.6	-2	5.5 (-11)	-10.4	-3	1.3 (-10)	

<sup>a</sup>Alkyl radical + Cl<sub>2</sub> rate constants and Arrhenius parameters from ref 24. HCO + Cl<sub>2</sub> entries from this study. <sup>b</sup>Alkyl radical + Br<sub>2</sub> rate constants and Arrhenius parameters from ref 46. HCO + Br<sub>2</sub> entries from this study. <sup>c</sup>Ionization potentials from ref 52. <sup>d</sup>Numbers in parentheses indicate power of 10, e.g., 2.1 (-12) indicates  $2.1 \times 10^{-12}$ .

values obtained at the same temperature in recent studies, particularly with those from investigations in which this reaction was also essentially isolated:  $5.6 \times 10^{-12}$  (Shibuya et al.),<sup>5</sup>  $5.6 \times 10^{-12}$ (Veyret and Lesclaux),<sup>7</sup> and  $5.1 \times 10^{-12}$  (Temps and Wagner).<sup>10</sup> (Rate constants in this discussion are in units of cm<sup>3</sup> molecule<sup>-1</sup> s<sup>-1</sup>.)

A very small increase in  $k_2$  with temperature (corresponding to an Arrhenius activation energy of only  $1.7 \pm 1.5$  kJ mol<sup>-1</sup>) was observed over the temperature range of our study of reaction 2 (295-713 K). Veyret and Lesclaux observed a minor decrease in  $k_2$  between 298 and 503 K.<sup>7</sup> The measured values of  $k_2$  from both studies do, however, lie within each other's stated uncertainties over the temperature range covered in both studies with the exception of the highest common temperature (see Figure 2).

The difference in temperature dependencies of  $k_2$  observed in these two investigations has some importance if the results of either study are extrapolated to much higher temperatures (e.g., up to 2000 K) for use in modeling combustion chemistry. Warnatz has reviewed direct and indirect determinations as well as estimates of  $k_2$  and suggested a temperature independent value of  $5 \times 10^{-12}$ for use in combustion modeling.<sup>3</sup> A small adjustment (to  $7 \times$ 10<sup>-12</sup>) would represent an improvement in this recommendation since it takes into account the results of both the current and the prior investigation of the temperature dependence of  $k_2$ .

2. Reaction Mechanisms. The mechanisms of reactions 2-5 could not be confirmed (in the cases of reactions 4 and 5) or established (in the case of reaction 3) through direct detection and monitoring of possible product ion signals for the reasons described in the previous section. However, as mentioned in the Introduction, the mechanisms of reactions 2, 4, and 5 have been established by others.<sup>10,20-22</sup> It is likely that the mechanism of reaction 3 begins with an addition process, a behavior which has been noted for other  $R + NO_2$  reactions.<sup>32-35</sup> Two reactive routes are possible:

> $HCO + NO_2 \rightarrow HCO_2 (H + CO_2) + NO_2 (H + CO_2$ (8)

or

$$HCO + NO_2 \rightarrow HNO_2 + CO$$
 (9)

A comparable mechanism to reaction 8 was identified in an earlier investigation of the CH<sub>3</sub>CO + NO<sub>2</sub> reaction, and its rate constant at 295 K  $(2.5 \times 10^{-11})$  is within a factor of 2 of that of the HCO + NO<sub>2</sub> reaction at this temperature.<sup>36</sup> Reaction 3 would begin with the formation of an energy-rich HCO-NO2 adduct which subsequently rearranges by internal H-atom migration before decomposition occurs to form the ultimate products.

3. Reactivity of HCO. There is increasing evidence that exothermic reactions between carbon-centered free radicals and the halogen molecules (Cl<sub>2</sub>, Br<sub>2</sub>, and I<sub>2</sub>) proceed largely without energy barriers.<sup>24,37-39</sup> and that reactivity in such cases is determined largely by the magnitudes of the long-range forces between the reactants (as is the case in well-known families of addition reactions, e.g., O + olefin,<sup>40</sup> OH + olefin,<sup>41</sup> and alkyl radicals +  $O_2^{42}$ ).

There has been success in correlating the rate constants of elementary reactions which have minimal or no energy barriers along their reaction coordinate with molecular parameters that reflect the magnitudes of the attractive dispersion forces between the reactants. Linear relationships have been reported between activation energies (or  $\log k$  at a fixed temperature) and the ionization potential (IP) of the free radical (or the stable molecular reactant),<sup>43-46</sup> the inverse of the polarizability of the stable molecular reactant,44 or IP - EA (the difference between the ionization potential of the free radical and the electron affinity (EA) of the molecular reactant).<sup>42,47</sup> The first two parameters are useful for accounting for trends in reactivity within a group of reactions in which one reactant is the same, and the third has, in addition, been used to draw together (sometimes to near coalescence) the dependence of the rate constants (at a fixed temperature) of various series of reactions involving different stable molecular reactants into a common dependence on (IP - EA).<sup>42</sup>

The reactivity of the formyl radical fits well into these correlation schemes. HCO has an ionization potential between that of CH<sub>3</sub> and C<sub>2</sub>H<sub>5</sub> and a reactivity in  $R + Cl_2$  and  $R + Br_2$ reactions which is likewise between that of these two alkyl radicals. See Table II. (The reactivity differences among the  $R + Br_2$ ) reactions is less apparent since all are extremely rapid.) Higher rate constants for the HCO +  $Br_2$  reaction (compared to those of the HCO +  $Cl_2$  reaction at the same temperatures) are also expected. The slightly higher electron affinity of Br<sub>2</sub> compared to Cl<sub>2</sub> (2.55 eV compared to 2.4 eV)<sup>48</sup> and the higher polarizability of Br<sub>2</sub> compared to Cl<sub>2</sub> (69.9 cm<sup>3</sup> compared to 46.1 cm<sup>3</sup>)<sup>49</sup> are both indicators of longer range dispersion forces between HCO and  $Br_2$  than between HCO and  $Cl_2$ .

4. Heterogeneous Effects. A concern in studies of the type described in this paper is the effect of possible "hidden" heterogeneous processes on the interpretation of the experimental results. The heterogeneous loss of HCO in the absence of the second reactant is measured ( $k_{\rm B}$  in Table I) and is taken into account in the data analysis used to obtain the rate constant of the homogeneous HCO reaction under investigation. Additional heterogeneous loss of HCO in the presence of the molecular reactant which has a rate that is proportional to the concentration of this

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added reactant is difficult to detect. A failure to take such a process into account in the data analysis, if it is present, would result in calculated homogeneous rate constants which are too large. Since adsorption of the molecular reactant on the reactor wall would be more important at lower temperatures, such heterogeneous processes would also result in larger errors at low temperatures than at higher ones. So, in addition to yielding higher rate constants, such interference from bimolecular heterogeneous processes would also yield lower activation energies, even negative ones where the actual activation energy is small or zero.

Directly establishing the absence of such heterogeneous reactions involves observing an independence of the measured rate constants on the surface/volume ratio of the reactor and/or on the reactor wall condition. Less directly, obtaining agreement (particularly at the lower temperatures of the study) with other investigations which have isolated the same reaction for quantitative study under conditions where heterogeneous reactions cannot occur is a strong indication that heterogeneous processes are unimportant. Using our current apparatus, it is not possible to alter the reactor size. So the first test cannot be performed. Early experiments were done using an uncoated reactor. These conditions produced higher values of the first-order wall rate constant  $(k_{\rm B})$ , the intercept of the plot of k'vs [molecular reactant]. These experiments were considered of lower precision than those reported in this paper, ones in which a boric acid coated reactor was used. Nevertheless, these early experiments did yield rate constants which were the same as those obtained by using the boric acid coated tube. We are in the process of developing Teflon coatings for our reactors which will be used in future studies to provide significantly different wall conditions to conduct such tests more reliably. There is excellent agreement between the HCO +  $O_2$ rate constant measured in the current study at ambient temperature and those obtained in earlier direct studies of this reaction, which indicates, for this reaction at least, that no heterogeneous bimolecular reaction between HCO and O<sub>2</sub> occurred under our experimental conditions.

A theoretical assessment of the possible importance of bimolecular heterogeneous reactions under our experimental conditions is also possible. It begins, in this case, with the prior knowledge that only a sparse coverage of the reactor surface with the molecular reactant would yield a coverage and heterogeneous reaction rate which is proportional to the gas-phase concentration of the molecular reactant (and hence pass undetected in these experi-

ments). The extent of wall coverage must be exceptionally small under the conditions of the current study. For example, at the typical Br<sub>2</sub> gas densities used in this study  $(3 \times 10^{12} \text{ molecules})$ cm<sup>-3</sup>), just 1% wall coverage would require a heat of adsorption of over 20 kcal/mol.<sup>50</sup> A coverage of greater than this magnitude would be required to yield a heterogeneous reaction rate which would affect the results of this study, because the homogeneous reaction already proceeds without an energy barrier.<sup>51</sup> The heterogeneous reaction cannot inherently be a faster process than the homogeneous one. If a reactant such as Br<sub>2</sub> were held to the surface with a binding energy of over 5-10 kcal/mol, there would be a major reduction in its extent of coverage with a slight increase in temperature. If a bimolecular heterogeneous reaction were an important process in these experiments, it would manifest itself as an apparent homogeneous reaction rate constant which decreased dramatically with increasing temperature at the lowest temperatures of the study, but which had a significantly different temperature dependence at the higher temperatures. This behavior was not observed in the temperature dependencies of the rate constants associated with the reactions studied. For reactions 2-5, the temperature dependencies were not only slight but also were essentially uniform over the significant temperature ranges covered in these studies.

On the basis of the observations and considerations presented here, we conclude that bimolecular heterogeneous processes did not occur to a detectable extent under the experimental conditions of this study.

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**Registry No.** HCO, 2597-44-6; O<sub>2</sub>, 7782-44-7; NO<sub>2</sub>, 10102-44-0; Cl<sub>2</sub>, 7782-50-5; Br<sub>2</sub>, 7726-95-6; MeCHO, 75-07-0.

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