Experimental Investigation of the Reaction between Nitric Oxide and Ketenyl Radicals (HCCO + NO): Rate Coefficient at T = 290-670 K and Product Distribution at 700 K

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The HCCO + NO reaction (r5) was investigated in $C_2H_2/O/NO$ systems at a pressure of 2 Torr (He bath gas) using discharge flow-molecular beam mass spectrometry techniques (DF-MBMS). The first rate coefficient data at temperatures > 300 K are presented. The coefficient was measured relative to the known k(HCCO+O)from the change of steady-state HCCO signals upon adding increasing amounts of NO. Thus, in the temperature range from 290 to 670 K, the k(HCCO+NO) coefficient was found to exhibit a slight but significant temperature dependence: $k(T) = (1.0 \pm 0.3) \times 10^{-10} e^{-(350 \pm 150)/(T/K)} cm^3 molecule^{-1} s^{-1} (T = 290-670 \text{ K})$. The product distribution was determined at 700 K. The experiments relied on the fact that all reaction pathways yield either CO or CO₂. Ketenyl radicals, generated by quantitative reaction of a known amount of O atoms with C_2H_2 in high excess, were reacted with a large excess of NO, ensuring quantitative conversion into the products CO₂ and CO. The product distribution was essentially deduced from the ratios [CO₂]_{formed}/[O]_{input} and [CO]_{formed}/ $[O]_{input}$. Formation of CO together with $CH_2(^3B_1)$ in a minor (25 ± 15%) channel of the C_2H_2 + O reaction was taken into account. Small corrections for secondary reactions such as $HCCO + O \rightarrow H + 2CO$ were made by kinetic modeling. Thus, the following yields were obtained: for HCCO + NO \rightarrow (CHNO) + CO, 77 ± 9%; for HCCO + NO \rightarrow (CHN) + CO₂, 23 ± 9%. Strong product signals were also observed at m/e = 43and m/e = 27, confirming that CHNO isomers and CHN isomers are formed along with CO and CO₂, respectively. Theoretical predictions regarding the CO/CO_2 yield ratio, presented in a companion paper in this issue, can be reconciled with the experimental product distribution only when an as yet unidentified entrance pathway to the formyl isocyanate intermediate is assumed to exist and to be thermally accessible.

Introduction

The awareness that combustion-generated NO emissions from both stationary and mobile sources are at the base of the formation of urban ozone and other harmful photooxidants has given rise to intensive research on NO chemistry in combustion processes.

Nitric oxide formation in flames is now qualitatively well understood. Regarding the abatement of NO_x emissions, much of the research effort is focused on the capacity of additives to reduce NO in the postflame region (thermal $DeNO_x^{-1}$ and RAPRENO_x² processes). On the other hand, in order to understand and control NO emissions adequately, kinetic data on the so called "natural" NO destruction processes are also required. NO consumption in flames is known to take place through reaction with NH₂ and with hydrocarbon radicals such as C, CH, CH₂, CH₃, The promising alternative "NO reburn" strategy for abatement of NO_x emissions is actually based on such reactions. This process involves a staged combustion, where a hydrocarbon fuel added in the second, fuel-rich stage provides hydrocarbon radicals which can react with and finally reduce the NO formed in the first, fuel-lean stage. However, rate constant and product distribution data on many NO destruction pathways are still lacking. A potentially crucial reaction in this context-which has received insufficient attention so far-is NO removal by HCCO radicals, known to be produced in the oxidation of ethyne by atomic oxygen:

$$C_2H_2 + O \rightarrow HCCO + H$$
 (r1a)

$$\rightarrow CH_2(^3B_1) + CO$$
 (r1b)

Although the branching ratio of this reaction has long been a matter of controversy, recent measurements, including work by our group, have unambiguously shown that the HCCO + H path

is the major product channel, accounting for $60-85\%^{3-7}$ of the primary products. Consequently, given also the low rate constant for HCCO removal by $O_{2,3,8-10}$ the HCCO + NO reaction might be a dominant NO reduction path in C_2H_2 -based reburn processes. Only recently, the results of two room temperature studies on the HCCO + NO reaction were published. Unfried et al.⁸ monitored the real-time decay of HCCO by use of infrared absorption spectroscopy under pseudo-first-order conditions and obtained a rate constant of 3.9×10^{-11} cm³ molecule⁻¹ s⁻¹, they produced HCCO by 193-nm photolysis of ketene. Temps et al.⁹ in their far infrared laser magnetic resonance (FIR-LMR) study used the reaction of O atoms with C_2H_2 as a HCCO source and in similar pseudo-first-order experiments found a somewhat lower rate constant of 2.2×10^{-11} cm³ molecule⁻¹ s⁻¹.

The first objective of the present study is to measure the rate constant of this reaction over an extended temperature range, in order to allow a reliable estimate at flame temperatures.

In addition it is imperative to investigate the HCCO + NO reaction with respect to the nature and distribution of the reaction products. From thermochemical considerations one finds that the reaction can result in a variety of N-containing species, i.e. CHNO isomers, CHN isomers, or NCO, together with CO, CO₂, or HCO (ΔH_r values from refs 11 and 12):

HCCO + NO → HCN + CO₂
$$\Delta H_r = -126 \text{ kcal/mol}$$

(r5a)
→ HNC + CO₂ $\Delta H_r = -110 \text{ kcal/mol}$
(r5b)
→ HCNO + CO $\Delta H_r = -48 \text{ kcal/mol}$
(r5c)
→ HNCO + CO $\Delta H_r = -116 \text{ kcal/mol}$
(r5d)

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Experimental Study of the HCCO + NO Reaction

→ HONC + CO
$$\Delta H_r = -35 \text{ kcal/mol}$$

(r5e)
→ HOCN + CO $\Delta H_r = -94 \text{ kcal/mol}$
(r5f)

$$\rightarrow$$
 NCO + HCO $\Delta H_r = -17 \text{ kcal/mol}$
(r5g)

With the CHNO isomers converted to HCN through subsequent flame reactions with H, O, and OH, it follows that a fast HCCO + NO reaction will induce NO reduction through the wellestablished mechanism:

$$HCN \xrightarrow{O} NCO \xrightarrow{H} NH \xrightarrow{H} N \xrightarrow{NO} N_2$$

Formation of HNCO, in channel r5d, would lead to more direct NO reduction via the sequence

$$HNCO \xrightarrow{H} NH_2 \xrightarrow{NO} N_2$$

In other words, the knowledge of the reaction products of HCCO + NO is also required to establish the mechanism that describes the resulting NO chemistry completely. To our knowledge, no product study of HCCO + NO has been reported so far. Hence, the second objective of this work is to identify and quantify its dominant channels.

Experimental Section

The discharge-flow reactor-molecular beam mass spectrometry apparatus (DF-MBMS) used in the present work has been described previously.¹³ Only the main characteristics are given here. Basically, the flow reactor consists of a cylindrical quartz tube (i.d. = 15.6 mm) equipped with a microwave discharge and an axially movable central injector tube. Oxygen or hydrogen atoms are generated in a microwave discharge from O₂ or H₂ diluted in helium as the carrier gas. C₂H₂ and NO, diluted in He, were added through the central injector. All experiments were carried out at a total reactor pressure of 2 Torr (He) and at T = 290-700 K. A heating mantle around the reactor tube ensures a uniform temperature. Linear flow velocities—depending on temperature—ranged from 20 to 45 m/s, with corresponding maximum reaction times of 12 and 5 ms, respectively.

Qualitative and quantitative analysis of the investigated reaction mixtures was carried out by molecular beam sampling and mass spectrometric detection. Sampling occurs downstream of the reactor through a 0.3-mm pinhole in a hollow quartz cone, giving access to the first of two differentially pumped low-pressure chambers. In the first stage the gas jet is mechanically chopped to allow phase sensitive detection. The resulting modulated molecular beam then enters the second low-pressure chamber which houses an electron impact ionizer and a Extranuclear Laboratory quadrupole mass spectrometer. CO, CO₂, m/e = 27CHN isomers, and m/e = 43 CHNO isomers were monitored at electron energies of 38 eV. Atoms and radicals were ionized at electron energies only a few electronvolts above the ionization potentials (see Table 1). When measuring CO concentrations, the m/e = 28 signals were corrected for CO⁺ fragment ions from CO₂. HCCO and CO₂ signals were corrected for isotope contributions from respectively the C_3H_4 and m/e = 43 CHNO species.

Commercial certified mixtures were used to obtain absolute concentration data for C_2H_2 , O_2 , H_2 , NO, CO, and CO₂. Calibration of O and H atoms was achieved by the well-known "discharge on-off" method. All reagents used are listed in Table 2. They were used without further purification except for C_2H_2

The Journal of Physical Chemistry, Vol. 98, No. 33, 1994 8037

TABLE 1: Selected Electron Energies

			-		
species	$E_{ m el}/ m eV$	species	$E_{ m el}/ m eV$	species	$E_{\rm el}/{\rm eV}$
Н	15.3	CO	38.0	(CHNO)	38.0
0	15.3	O2	68.0	CO ₂	38.0
C_2H_2	14.3	C₃H₄	12.0		
(CHN)	38.0	HCCO	12.0		

 TABLE 2: Reactant Gases and Certified Calibration Gas

 Mixtures

gas (mixture)	purity	supplier	
He N45	99.995%	UCAR	
He N56	99.9996%	UCAR	
C_2H_2	1.95% in He N56	UCAR	
C_2H_2	99.6%	SOGAZ	
H_2	2.39% in He N56	UCAR	
O2	10.1% in He N56	UCAR	
NO	10.0% in He N56	UCAR	
CO	99.99 7%	L'Air Liquide	
CO ₂	1.00% in He N45	Chemogas	

(99.6%), which was led through an acetone/dry ice bath to remove acetone.

Rate Constant of the HCCO + NO Reaction at T = 290-670 K

1. Methodology. The measurement of the rate constant of HCCO + NO was carried out in C_2H_2/O systems, where the HCCO radical is known to be the dominant primary product. A *direct* determination of k(HCCO+NO) in such a system is hampered by the competing HCCO destruction reactions with O and H atoms. The latter arise, *e.g.*, as the companion product of the primary HCCO radicals. Therefore, experiments were designed to measure the above rate constant relative to the known kinetic coefficient of the HCCO + O reaction.^{6,10} Basically, the method involves measuring the relative change of steady-state HCCO signals in $C_2H_2/O/NO$ systems upon changing the [NO]/[O] ratio.

The HCCO chemistry in C_2H_2/O systems is well established,³⁻¹⁰ comprising formation in the primary step—to our knowledge there is no evidence whatsoever for other HCCO sources of any importance—and destruction through reaction with O and H atoms and O₂ molecules:

$$C_2H_2 + O \rightarrow HCCO + H$$
 (rla)

 $HCCO + O \rightarrow products$ (r2)

$$HCCO + H \rightarrow products$$
 (r3)

$$HCCO + O_2 \rightarrow products$$
 (r4)

The total rate coefficient of reaction r1 is well-known over a large T range. From a recent survey⁵ of the available data, one finds that for T = 290-700 K it is well expressed by $k_1 = 3.1 \times 10^{-11}$ exp[-(1630/T)] cm³ molecule⁻¹ s⁻¹. The above HCCO removal processes have been studied intensively in the past, in this laboratory, among others, at temperatures of 287 K up to 535 K. In this range, the rate coefficient of the HCCO + O reaction was found to be^{3,10}

$$k_2(T) = (1.8 \pm 0.2) \times 10^{-10} e^{[(200\pm100)((1/535)-(1/T))]} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The high-temperature (1500–2500 K) shock tube determination by Frank et al.,⁶ $k_2 = 1.7 \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹, is in accord with our results; it differs by less than 30% from the (far) extrapolation of the above expression. It is important to note also that our room temperature k_2 value of 1.3×10^{-10} is in excellent agreement with that based on the linear correlation

TABLE 3: Temperatures, Initial Mixture Compositions, Added [NO] Ranges (all 10^{13} molecules cm⁻³), Flow Velocities, and Reaction Times at Which k_5/k_2 Was Measured

T (K)	[C ₂ H ₂] ₀	[O]₀	[O ₂]	[NO] ₀	v (m s ⁻¹)	time (ms)
290	32.3	6.2	30	0.0-93.5	19	3.2
400	18.2	7.0	35	0.0-89.2	22	2.3
530	16.1	4.0	29	0.0-72.1	34	1.8
670	12.5	4.5	29	0.0-37.7	44	1.4

TABLE 4: Determination of k_5/k_2 . Experimental Data at Each of the Investigated Temperatures^a

[NO]	[C ₂ H ₂]	[O]	[H]	[O ₂]	<i>i</i> HCCO
	7	= 290 K, I	= 3.2 ms		
0.00	31.8	4.72	0.87	30	116.7
13.4	26.5	4.36	0.64	30	75.2
28.0	27.0	4.19	0.54	30	39.5
40.9	25.8	3.79	0.54	30	28.5
60.0	24.2	3.89	0.47	30	24.8
74.4	24.0	3.25	0.40	30	18.3
93.5	24.1	3.28	0.37	30	13.5
	7	= 400 K, a	t = 2.3 ms		
0.00	16.4	4.08	1.31	35	237
9.72	15.5	4.50	1.26	35	152
18.6	15.0	4.45	1.14	35	127
28.0	14.8	4.45	0.83	35	101
39.0	14.5	4.42	1.05	35	77
56.1	14.0	4.74	1.00	35	55
73.4	13.6	4.33	0.92	35	45
89.2	13.3	4.30	0.90	35	37
	T	= 530 K, a	t = 1.8 ms		
0.00	13.6	2.27	1.90	29	366
6.75	13.2	2.36	1.81	29	306
20.3	13.2	2.43	1.74	29	190
29.2	12.3	2.45	1.68	29	149
43.7	12.1	2.36	1.65	29	117
58.0	12.2	2.25	1.65	29	83
72.1	11.9	2.29	1. 6 1	29	65
	T	= 670 K, t	t = 1.4 ms		
0.00	10.6	1.64	1.32	29	490
5.87	9.86	1.52	1.10	29	338
11.4	9.74	1.55	1.09	29	260
18.8	9.72	1.48	1.03	29	199
27.2	10.0	1.49	0.96	29	147
37.7	9.22	1.42	0.91	29	102

^{*a*} All concentrations are in 10^{13} molecules cm⁻³; i_{HCCO} is in arbitrary units.

between log k(R+O) and the ionization potential IP of the radical R, observed for alkyl and acyl radicals as well as resonancestabilized unsaturated radicals.¹⁴ On that basis, using IP(HCCO) = 9.5 eV,¹¹ one expects $k_2 = 1.4 \times 10^{-10}$.

The rate constant ratio k_3/k_2 was determined as such by Vinckier et al.:¹⁰ $k_3/k_2 = 1.3 \pm 0.2$ at 287 K and 1.4 \pm 0.4 at 535 K. Frank et al.⁶ reported a shock tube k_3 determination of about 2.5 $\times 10^{-10}$ cm³ molecule⁻¹ s⁻¹ at 1500–2500 K. Combining this with their k_2 result⁶ leads to $k_3/k_2 = 1.5$ at $T \approx 2000$ K, fully in the line of our k_3/k_2 data at 287 and 535 K.

In the conditions of the present experiments (see Tables 3 and 4), the HCCO removal frequency by reactions r2 and r3 together is between 5000 and 10000 s⁻¹.

A k_4/k_2 rate constant ratio measurement was reported by Peeters et al.,³ also in the T = 287-535 K range; in combination with the k_2 expression^{3,10} above, it yields $k_4(T) = 2.7 \times 10^{-12}$ exp[-430/(T/K)] cm³ molecule⁻¹ s⁻¹, with a 2σ error of ~30%. Recently, two direct studies on HCCO + O₂ at room temperature were published; Murray et al.¹⁵ obtained a k_4 value of 6.5×10^{-13} cm³ molecule⁻¹ s⁻¹, in excellent agreement with our $k_4(295\text{K})$ value of 6.3×10^{-13} cm³ molecule⁻¹ s⁻¹ from the above temperature relation.³ Temps et al.,⁹ using C₂H₂ + O as a HCCO source, measured a k_4 value of 2.2×10^{-13} cm³ molecule⁻¹ s⁻¹; their observed HCCO decay rate might have been low due to HCCO regeneration via reaction of the O atoms produced⁹ by HCCO $+ O_2 \rightarrow HCO + CO + O$ with the excess C_2H_2 .

On the basis of the $k_4(T)$ expression above, the HCCO + O_2 reaction is found to account for 3-6% of the total HCCO loss in the present experiments; although fairly unimportant, the reaction was retained in the mechanism.

Reaction of HCCO with C_2H_2 , the only other major species in C_2H_2/O systems, is negligibly slow. The highest reported values of the upper limits of $k(HCCO+C_2H_2)$ are $\leq 10^{-13}$ at room temperature, by Murray et al.,¹⁵ and $\leq 5 \times 10^{-13}$ at 535 K, by Vinckier et al.¹⁰ Thus, the upper limit of the HCCO destruction frequency by the reaction with C_2H_2 in the present experiments is $<30 \text{ s}^{-1}$ at 290 K and $<90 \text{ s}^{-1}$ at 670 K. These upper limits are less than 2% of the HCCO loss rate by reactions 2 and 3; therefore the reaction with C_2H_2 need not be considered in the investigated systems.

From earlier studies³ in this laboratory it also follows that destruction of HCCO on the quartz reactor walls proceeds at a rate of at most 35 s^{-1} at T = 535 K, which is likewise negligible versus the 5000–10000-s⁻¹ removal frequency due to reactions 2 and 3.

One can therefore conclude that, in the absence of NO, only the HCCO destruction reactions r2 and r3 actually matter (the HCCO + O_2 reaction being of only minor importance). Moreover, it will be shown below that in the determination of the rate contant of the HCCO + NO reaction relative to k_2 , the only other kinetic parameter of importance is the ratio k_3/k_2 , which is known.

The present k_5/k_2 measurements were carried out on C_2H_2/O systems where $k_1[C_2H_2] \ll k_2[O]$, such that quasi-steady state is established for HCCO at reaction times $t \gg 1/\{k_2[O]\}$. When adding NO to such a system, the additional HCCO consumption by

$$HCCO + NO \rightarrow products$$
 (r5)

will lead to a change of the steady-state HCCO concentration at any given time t:

$$[\text{HCCO}]_{\text{st}} = \frac{k_{1a}[\text{C}_2\text{H}_2][\text{O}]}{k_2[\text{O}] + k_3[\text{H}] + k_4[\text{O}_2] + k_5[\text{NO}]} \quad (1)$$

The addition of NO can also alter the concentration of the other reactive species. Due to the competition between O, H, and NO for HCCO, the presence of NO could result in a decreased O and H consumption. On the other hand, the products of these NO reactions may open up additional O and H destruction pathways. The presence of other reactive intermediates, such as $CH_2(^{3}B_1)$, induces similar changes. Finally, NO may enhance the wall termination of both O and H atoms. To account for these secondary effects, the actual, C_2H_2 , O, H, and O_2 concentrations at time t were remeasured for each of the NO concentrations. In this way, any change of concentration of a reactant—whatever the cause—is duly taken into account. The complete experimental data set, for each temperature, is given in Table 4.

Returning to eq 1, since HCCO + O is the most important removal path in the absence of NO, it is obvious that the rate constant of the HCCO + NO reaction should be derived relative to the known rate coefficient k_2 . With replacement of [HCCO]_{st} by its mass spectrometric signal i_{HCCO} , the steady-state equation can be rearranged as

$$\frac{[C_2H_2][O]}{i_{HCCO}\left([O] + \frac{k_3}{k_2}[H] + \frac{k_4}{k_2}[O_2]\right)} = \frac{k_2S_{HCCO}}{k_{1a}}\left(1 + \frac{k_5}{k_2}\frac{[NO]}{\left([O] + \frac{k_3}{k_2}[H] + \frac{k_4}{k_2}[O_2]\right)}\right) (2)$$

where S_{HCCO} is the mass spectrometric sensitivity.

The straightforward reason for the rearrangement is that the validity of the steady-state expression written in this alternative form can be directly inspected, visually: a plot of the left-hand side of eq 2 versus the quantity $[NO]/\{[O] + k_3/k_2[H] + k_4/k_2[O_2]\}$ (further denoted by X) should yield a straight line. Furthermore, the slope to intercept ratio of this straight line directly provides k_5/k_2 . It is clear that the constant k_2S_{HCCO}/k_{1a} need not be known since it is common to both the slope and the intercept.

It must be stressed that the ratio k_3/k_2 is the only important kinetic parameter required to derive k_5/k_2 . Indeed, as already noted above, the contribution of the $(k_4/k_2)[O_2]$ term is very small versus $\{[O] + (k_3/k_2)[H]\}$. That the ratio k_3/k_2 of the rate constants of the dominant competing HCCO removal reactions is indeed known satisfactorily was already shown above. In addition, it should be noted that in our experimental conditions $(k_3/k_2)[H]$ accounts on average for only 50% of the denominator of both the left-hand side and of the quantity X in eq 2. This implies that an uncertainty on k_3/k_2 of as much as 30% results in uncertainties on the left-hand side and on X of only 15%.

The value for k_3/k_2 in eq 2, at T = 290-670 K, was taken to be 1.53 exp[-45/(T/K)], which fits the experimental data 1.3 at 287 K,¹⁰ 1.4 at 535 K,¹⁰ and 1.5 at 1500-2500 K.⁶ The unimportant parameter k_4/k_2 was evaluated from $k_4/k_2(T) =$ $1.0 \times 10^{-2} \exp[-230/(T/K)]$, as can be found from the data reported by Peeters et al.³ for T = 287-535 K.

2. Results. Measurements were carried out on four C_2H_2/O mixtures, at temperatures of 290, 400, 530, and 670 K, respectively, at a total pressure of 2 Torr, with helium as the bath gas. No indication was found for the presence of a possible HCCO + NO combination product at m/e = 71, even at low temperatures. Moreover, the theoretical companion study¹⁸ shows that the rate of the HCCO + NO reaction is determined by the initial combination steps; indeed, the energies of each of the predicted initial intermediates and of the lowest subsequent transition structures are such that the ensuing isomerization and decomposition steps will be much faster than redissociation back to the reactants and than collisional stabilization. Hence, there is no reason to expect any pressure dependence. Accordingly, the present study was limited to a single pressure.

The initial mixture compositions, added [NO] ranges, flow velocities, and reaction times at the moment of measurement are listed in Table 3. The initial $[C_2H_2]_0/[O]_0$ ratio was chosen sufficiently high for reasons clarified below. The reaction time *t* ranged from 1.4 to 3.2 ms, depending on temperature. At the prevailing, high $[O]_0$, the HCCO destruction frequency is close to 10^4 s⁻¹, ensuring establishment of the HCCO quasi-steady state long before the actual reaction time at which HCCO is monitored. Kinetic modeling⁷ shows that in the experimental conditions the true [HCCO] deviates less than 5% from its local steady-state value.

As shown in Table 1, HCCO signals were monitored at ionizing electron energies of 12.0 eV. The m/e = 41 signals were duly corrected for small (<5%) contributions of the ¹³C isotope of C₃H₄, formed in C₂H₂/O systems. To that end, m/e = 40 signals were recorded in identical conditions. High $[C_2H_2]_0/[O]_0$ ratios and fairly short reaction times were chosen here to suppress the secondary reactions known to cause C₃H₄ formation.^{16,17} Along with i_{HCCO} , also the absolute concentrations of C₂H₂, O, O₂, and H were measured for each [NO] at the reaction time of interest.

Figure 1 shows the eq 2 plots which were obtained at each of the experimental temperatures. The high correlation coefficients $r \ge 0.99$ for each of the linear regression lines are witness to the validity of the equation. The k_5/k_2 values, equal to the slope/ intercept ratios, together with the k_5 results derived by using the literature k_2 values,^{3,10} are summarized in Table 5. The indicated errors correspond to the 95% confidence intervals; they include



Figure 1. Determination of k_5/k_2 from eq 2 at the four experimental temperatures: plot of the left-hand side versus the quantity X.

TABLE 5: Experimental k_5/k_2 Ratios, Literature k_2 Values,^{3,10} and the Derived k_5 Rate Coefficients at the Four Experimental Temperatures (95% Confidence Limits)

-		· ·	
T (K)	k_{5}/k_{2}	k_2 (cm ³ molecule ⁻¹ s ⁻¹)	k_5 (cm ³ molecule s ⁻¹)
290	0.23 ± 0.11	$(1.31 \pm 0.45) \times 10^{-10}$	$(3.1 \pm 1.8) \times 10^{-11}$
400	0.31 ± 0.06	$(1.59 \pm 0.44) \times 10^{-10}$	$(4.9 \pm 1.7) \times 10^{-11}$
530	0.33 ± 0.10	$(1.79 \pm 0.47) \times 10^{-10}$	$(5.8 \pm 2.4) \times 10^{-11}$
670	0.32 ± 0.06	$(1.94 \pm 0.52) \times 10^{-10}$	(6.1
	-22 In k ₅ -23	; 	
	-24		
	-25		
	26		1/T
	0.001	0.002 0.003	0.004
	0.001	0.002 0.003	0.004

Figure 2. Arrhenius plot for the rate coefficient k_5 of HCCO + NO, at T = 290-670 K.

the uncertainties on the respective intercepts and slopes and on the k_2 values^{3,10} but with an additional estimated systematic k_2 error of 15%.

The directly obtained k_5/k_2 data can be represented as $k_5/k_2 = (0.4 \pm 0.1) \exp[-(150 \pm 100)/(T/K)]$. The Arrhenius plot for k_5 in Figure 2 shows that the HCCO + NO rate coefficient exhibits a slight, positive temperature dependence:

$$k_5(T) = (1.0 \pm 0.3) \times 10^{-10} e^{-(350 \pm 150)/(T/K)} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$$

The 290 K value $k_5 = (3.2 \pm 1.8) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ is midway between the direct determinations $k_5 = (3.9 \pm 0.4) \times 10^{-11}$ by Unfried et al.⁸ and $k_5 = (2.2 \pm 0.7) \times 10^{-11}$ by Temps et al.⁹ This lends strong support to the soundness and consistency of our approach.

Product Distribution of the HCCO + NO Reaction at 700 K

The exoergic product routes of the HCCO + NO reaction, given in the Introduction, can be divided into three groups. Routes

r5a and r5b lead to an (CHN) isomer plus CO₂; (r5c)–(r5f) result in an (CHNO) isomer plus CO₂; (r5g) yields NCO plus HCO.

In the theoretical companion article,¹⁸ three possible entrance channels were discerned. The first is a simple, barrierless combination process forming nitrosoketene; the vibrationally excited HC(NO)CO[†] intermediate can either dissociate into CO plus HCNO or undergo electrocyclization followed by concerted expulsion of CO₂ and formation of HCN. A second entrance pathway leading to a stable aziridine derivative might also be thermally accessible; the three-membered ring easily decomposes to CO plus HNCO. The third and most stable intermediate that may arise directly from HCCO + NO is formyl isocyanate, localized at 112 kcal/mol below the reactants level; its most probable fate is facile fragmentation to HNCO plus CO, through a highly loose and low-lying transition structure. The only plausible path for route r5g, to HCO plus NCO, also proceeds through the formyl isocyanate intermediate. However, the above TS for extrusion of CO from HC(O)NCO lies far below the HCO + NCO products level: it must be concluded therefore that route r5g is negligibly slow compared to route r5d.

1. Procedure. A simplifying feature of the remaining reaction pathways is that they all lead to either CO or CO₂. This directed the design of our product distribution experiments. They relied on quantitative reaction of O atoms with excess C_2H_2 to form HCCO (together with $CH_2(^3B_1)$), followed by fast conversion of HCCO to CO or CO₂ by subsequent reaction with excess NO:

$$C_2H_2 + O \rightarrow HCCO + H$$
 (rla)

$$\rightarrow$$
 CH₂(³B₁) + CO (r1b)

$$HCCO + NO \rightarrow (CHN) + CO_2$$
 (r5a, 5b)

$$\rightarrow$$
 (CHNO) + CO (r5c-5f)

$$CH_2(^{3}B_1) + NO \rightarrow HCN + OH \qquad (70\%^{19}) \quad (r9a)$$

$$\rightarrow$$
 (CHNO) + H (r9b)

Ideal conditions ensuring quantitative conversion for both steps result in the following relations between the final amounts of CO and CO₂ produced and the initial $[O]_0$ in C₂H₂/O/NO systems:

$$\frac{[CO]_{f}}{[O_{0}]} = \frac{k_{1b}}{k_{1}} + \frac{k_{1a}}{k_{1}} \frac{k_{(5c-5f)}}{k_{5}}$$
(3)

$$\frac{[CO_2]_f}{[O]_0} = \frac{k_{1a}}{k_1} \frac{k_{(5a,5b)}}{k_5}$$
(4)

$$\{[CO_2]_f + [CO]_f\}/[O]_0 = 1$$
 (5)

Given that the k_{1a}/k_1 branching fraction is now well established at 0.75 ± 0.15 at T = 300-2000 K,³⁻⁷ a clear-cut strategy emerges to determine the contributions of the summed CO paths and the summed CO₂ paths of the HCCO + NO reaction.

The two conditions above can be met simultaneously by carrying out the experiments in reaction mixtures with a sufficiently high excess of both $[C_2H_2]_0$ and $[NO]_0$ compared to $[O]_0$; it is clear that the quantitative conversion of O into HCCO (and CH₂-(³B₁)) will be facilitated at elevated temperatures, where reaction r1 is greatly speeded up. High NO concentrations will force the primary products HCCO and CH₂(³B₁) to react mainly with NO. A high [NO] will therefore also suppress O removal by

TABLE 6: Initial Composition (10^{13} molecules cm⁻³) of the Seven C₂H₂/O/NO Mixtures for Product Analysis and Absolute [CO₂]_t and [CO]_t Measurd at t = 1.5 ms, T = 700 K, and p = 2 Torr in He Bath Gas

mixture	$[C_2H_2]_0$	[NO] ₀	[O] ₀	[CO ₂] _f	[CO] _f
1	75.9	69.2	2.11	.343	1.59
2	69.8	70.4	2.95	.427	2.32
3	88.5	74.6	3.25	.427	2.96
4	81.3	74.6	4.45	.560	4.45
5	80.7	78.3	4.70	.686	4.59
6	86.1	75.9	5.90	.807	5.62
7	106.6	95.1	7.34	1.10	7.37

secondary reactions such as (r2) and (r6), and at the same time it will drastically reduce "secondary" CO_2 and CO formation by

$$HCCO + O \rightarrow 2CO + H \tag{r2a}$$

$$\rightarrow$$
 CH(²II,⁴ Σ^{-}) + CO₂^{17,20,25} (r2b)

$$HCCO + O_2 \rightarrow CO_2 + HCO (H + CO)$$
 (r4a)

$$\rightarrow$$
 products (r4b)

$$CH_2(^{3}B_1) + O \rightarrow CO + 2H(H_2)$$
 (r6)

$$CH_2({}^{3}B_1) + O_2 \rightarrow CO_2 + H_2(2H)$$
 (r7a,b)

$$\rightarrow$$
 CO + H₂O (H + OH) (r7c,d)

The reduction of secondary CO and CO₂ from reactions 6 and 7 plays at two levels. First, NO directly competes with O and O₂ for CH₂(³B₁). Second, NO inhibits secondary CH₂(³B₁) formation, via HCCO + H \rightarrow CO + CH₂(¹A₁) and subsequent collisional deactivation of CH₂(¹A₁).^{7a} Indeed, at high [NO], removal of HCCO by NO will outrun that by H. The only fate of H will be reaction with C₂H₂ to form C₂H₃, which in the experimental conditions (p = 2 Torr of He and T = 700 K) remains very slow; in a separate study¹⁷ its rate constant was measured to be 3.5×10^{-14} cm³ molecule⁻¹ s⁻¹.

2. Results. In line with the considerations above, the product distribution was measured at a temperature of 700 K in mixtures with $[C_2H_2]_0 \approx [NO]_0 \approx (7-11) \times 10^{14}$ molecules cm⁻³ and $[O]_0 \approx (2-7) \times 10^{13}$ molecules cm⁻³. Total pressure was 2 Torr, with He as bath gas. Flow velocities were ~45 m s⁻¹. The initial reactant concentrations of the seven investigated $C_2H_2/O/NO$ mixtures are summarized in Table 6.

Absolute CO and CO₂ concentrations as well as mass spectrometric m/e = 43 signals (CHNO isomers) were measured. For some mixtures also the m/e = 27 signals (CHN) were monitored. The ionizing electron energy was 38 eV for all cases. CO₂ fragmentation to CO⁺ was duly taken into account. The CO and CO₂ concentrations were found to reach asymptotic values within less than 1 ms. Table 6 gives an overview of the measured absolute [CO] and [CO₂] concentrations at a reaction time of 1.5 ms.

Besides being of interest in its own right, the m/e = 43 signal was also required to correct for the ¹³C isotopic contribution to the m/e = 44 signal (¹³CHNO⁺).

No attempt was made to determine absolute CHNO and CHN concentrations. The main reason is the *a priori* possibility of different isomeric structures. Moreover, both CHN and CHNO also arise in the reaction of $CH_2(^{3}B_1)$ with NO.¹⁹ The signals of these species were recorded here only because of their qualitative interest as companion products of CO and CO₂. A thorough search for a possible HCCO + NO combination product at m/e = 71 was without result, even at lower temperatures.

 TABLE 7: Main Reactions (Sensitivity Coefficient ≥ 0.01) of the Mechanism for Kinetic Modeling Analysis of HCCO + NO

 Product Distribution Data

no.	reaction	rate constant at 700 K (cm ³ molecule ⁻¹ s ⁻¹)	ref
la	$C_2H_2 + O \rightarrow HCCO + H$	2.1×10^{-12}	3-7
1b	\rightarrow ³ CH ₂ + CO	7.0×10^{-13}	3–7
2a	$HCCO + O \rightarrow 2CO + H$	1.8×10^{-10}	10
2b	\rightarrow CH + CO ₂	2.1×10^{-11}	10, 17
3a	$HCCO + H \rightarrow {}^{1}CH_{2} + CO$	2.5×10^{-10}	10, 7a
4	$HCCO + O_2 \rightarrow CO_2 + products$	2.3×10^{-12}	10
5a-b	$HCCO + NO \rightarrow (CHN) + CO_2$	EA × 10-11	this work
5c-f	$HCCO + NO \rightarrow (CHNO) + CO$	§ 0.4 × 10 ···	
6	$^{3}CH_{2} + O \rightarrow CO + H_{2}/2H$	1.5×10^{-10}	13
7a-b	$^{3}CH_{2} + O_{2} \rightarrow CO_{2} + H_{2}/2H$	8.0×10^{-13}	24
7cd	\rightarrow CO + H ₂ O/OH + H	2.4×10^{-12}	24
9a	$^{3}CH_{2} + NO \rightarrow HCN + OH$	5.2×10^{-11}	19
9Ъ	\rightarrow (CHNO) + H	2.2×10^{-11}	19ª
23	$C_2H_2 + H \rightarrow C_2H_3$	3.5×10^{-14}	17
27	$C_2H_3 + NO \rightarrow products$	1.0×10^{-11}	estimate
35	$O \rightarrow wall$	50 s ⁻¹	

^a Temperature dependence of k_9 was assumed to be similar to k_5 .

For the quantitative determination of the products of the HCCO + NO reaction we relied on the absolute amounts of CO and CO₂ produced in the investigated $C_2H_2/O/NO$ mixtures. In principle, one can base the analysis on eqs 3 and 4 above. However, in some of the mixtures the effects of secondary O removal and CO and CO_2 production by reactions r2-r4, r6, and r7 cannot be entirely ignored. Whereas in mixtures 1-3 these effects amount to less than 5% of the O consumed or CO plus CO₂ formed, they account for up to 20% of the CO plus CO₂ in mixtures 6 and 7 with their higher [O]₀ values. Since the latter result in higher and hence very precise CO and CO₂ signals, we chose not to exclude these mixtures from the analysis. Rather, we opted for a kinetic modeling approach to derive the CO and CO₂ yields of HCCO + NO from the data, for all mixtures. It should be emphasized, however, that this does not imply at all that the product distributions are obtained here by "fitting a complex reaction mechanism". Rather, fairly small corrections on the analytical expressions 3 and 4 are made using an extended reaction scheme. To underscore this point, the raw CO and CO₂ yields derived directly from eqs 3 and 4 will also be given for each experiment to show the limited magnitude of the corrections (see Table 8).

The full reaction scheme comprises 35 reactions. Beside the reactions of direct interest to CO and CO₂ formation (r1-r7), it also contains all secondary, tertiary and relevant quaternary reactions that consume O, H, C₂H₂, O₂, and NO, in order to model the profiles of these major reactant species correctly. Table 7 lists reactions r1-r7 and in addition all the processes for which the sensitivity coefficients $\delta \ln[CO]/\delta \ln p_i$ or $\delta \ln[CO_2]/\delta \ln p_i$ were found to exceed 0.01; in these sensitivity coefficients expressions, the parameter p_i is either the rate constant k_i or the pertaining branching fraction (the latter for reactions r1, r2, r5, and r9). Figure 3 shows the sensitivity spectrum for the worst case, i.e. mixture 7; the sensitivity coefficients are expressed in percent. It can be appraised immediately from this bar chart that the absolute CO and CO_2 concentrations are dominantly controlled by the product distributions of the HCCO + NO reaction and of the primary $C_2H_2 + O$ reaction (where $p_i =$ k_{1a}/k_{1}).

The importance of k_{1a}/k_1 is obvious, as already expressed by the ideal-case equations (3) and (4). The uncertainty on this parameter largely determines the confidence interval of the present determination of the CO and CO₂ yields of HCCO + NO. Regarding the data on the other reactions that have some influence on CO/CO₂, we refer to the previous section (in the case of the rate constant of reaction r2 and r4) and to the references listed in Table 7. Only the CO₂ production in a minor channel of the HCCO + O reaction requires some further comment. This reaction was identified as the dominant CO₂ source in C₂H₂/O systems by modeling observed absolute CO₂ profiles.^{17,20,25} The



Figure 3. Absolute sensitivity coefficients of $[CO_2]$ and $[CO_2]$ in mixture 7, with respect to the model parameters of Table 7.

700 K k_{2b} value in Table 7 is based on a preliminary analysis of 300–900 K data, yielding $k_{2b}(T) = (5 \pm 2) \times 10^{-11} \exp[-(600 \pm 200)/(T/K)]$ cm³ molecule⁻¹ s⁻¹.

Thus, using the reaction mechanism partially displayed in Table 7, with $k_{1a}/k_1 = 0.75$, a best fit of the experimental [CO] and [CO₂] for all mixtures was obtained with the following branching fractions: $k_{5a-b}/k_5 = 0.23 \pm 0.03$ and $k_{5c-f}/k_5 = 0.77 \pm 0.03$; the indicated errors represent the statistical 95% confidence limits. Hence the CO₂- and CO-forming channels of the HCCO + NO reaction account for 23 ± 3 and $77 \pm 3\%$, respectively. Table 8 lists the experimental and the calculated [CO₂] and [CO]. It also contains the reaction r5 CO₂ and CO yields derived directly from analytical eqs 3 and 4. It can be noted in passing that in mixtures 1–3, where secondary reactions can be neglected; these uncorrected yields add up to an average of 95%.

The effect of possible systematic errors arising from uncertainties in the product distribution of the $C_2H_2 + O$ reaction must be verified. Its impact on the product distribution of HCCO + NO can be seen from eqs 3 and 4; a reduction of the importance of the HCCO plus H product channel will force the HCCO + NO reaction to higher CO₂ yields to meet the observed CO₂ productions. The six most recent data on k_{1a}/k_1 all range between 0.6 and 0.85,³⁻⁷ with only a slight temperature dependence between 300 and 2000 K, if any. We therefore repeated our model calculations with $k_{1a}/k_1 = 0.6$ and with $k_{1a}/k_1 = 0.85$. This changes the CO₂ yield to 29 ± 3 and 20 ± 2%, respectively.

Therefore, taking into account the possible systematic errors on k_{1a}/k_1 , one arrives at the following final result for the HCCO + NO product yields: $23 \pm 9\%$ for the CO₂ producing channels 5a and 5b; $77 \pm 9\%$ for the CO producing channels 5c-f.

TABLE 8:	Experimental	[CO ₂] and	[CO] Concentrations	(10 ¹³ molecules cm ⁻³) at $t = 1.5$	ms and Calculated '	Values Based on the
Parameter (Optimum k _{5a-b} /	$k_5 = 0.23$	and $k_{5c-f}/k_5 = 0.77$.	Uncorrected CO ₂ an	d CO Yields	from the Ideal-Cas	e Equations 3 and 4

mixture	[CO ₂] _{expt}	[CO ₂] _{calc}	[CO] _{expt}	[CO] _{calc}	uncorrected CO ₂ yield (%)	uncorrected CO yield (%)
1	0.343	0.301	1.59	1.75	21.7	67.2
2	0.427	0.409	2.32	2.44	19.3	71.4
3	0.427	0.476	2.96	2.78	17.5	88.1
4	0.560	0.608	4.45	3.81	16.8	93.0
5	0.686	0.650	4.59	3.99	19.5	96.9
6	0.807	0.759	5.62	5.10	18.2	93.7
7	1.10	0.993	7.37	6.50	20.0	100.

Discussion

The rate constant of the HCCO + NO reaction has been measured for the first time over an extended temperature range, T = 290-670 K. The $(3.2 \pm 1.8) \times 10^{-11}$ cm³ molecule⁻¹ s⁻¹ room temperature result is equal to the average of the available direct determinations: $k_5 = (3.9 \pm 0.4) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by Unfried et al.⁸ and $k_5 = (2.2 \pm 0.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ by Temps et al.⁹ Even though the 290 K value is the least precise of our measurements, the above underscores the reliability of our indirect approach.

The data in the T = 290-670 K range can be well represented by the Arrhenius expression $k_5(T) = (1.0 \pm 0.3) \times 10^{-10}$ $e^{-(350\pm150)/(T/K)}$ cm³ molecule⁻¹ s⁻¹. The high frequency factor and low Arrhenius activation energy $E_{act.} \simeq 0.7$ kcal/mol are both typical of a radical + radical reaction proceeding by (rate controlling) initial combination, i.e. by sharing the unpaired electrons.

To our knowledge, the products of HCCO + NO have been investigated here for the first time. As already noted, a complementary "ab initio" study has been carried out on this reaction.¹⁸ The major theoretical predictions, briefly repeated here, will be confronted with the experimental findings.

For the HCCO + NO reaction, three distinctive reaction pathways were characterized,18 proceeding respectively through nitrosoketene, an aziridine derivative, and formyl isocyanate. The main fate of the nitrosoketene intermediate is cyclization followed by decomposition to HCN and CO₂; only a small fraction of the HC(NO)CO is expected to decompose into HCNO + CO or into $HNC + CO_2$ because of the much higher barriers. The aziridine derivative can only yield HNCO + CO. Regarding formyl isocyanate, the transition states for subsequent fragmentation to HNCO + CO and HCN + CO_2 lie at the same level; however, due to the fact that the number of accessible vibrational states for the former transition structure is about 2 orders of magnitude larger, the formyl isocyanate pathway will predominantly result in HNCO + CO.

It must be added, however, that-possibly due to the complexity of the surface-the entrance pathways to the aziridine derivative and formyl isocyanate intermediates could not be identified, despite extensive attempts. It could only be surmised, on the basis of the high stability of the aziridine derivative and of formyl isocyanate (73 and 112 kcal/mol, respectively, below the reactant level), that one or both of these entrance paths exist and are nearly barrierless and therefore thermally as readily accessible as the path through nitrosoketene. Only when making this assumption can one bring the theoretical predictions in agreement with the experimental findings that CO production is far more important than CO₂ formation. In this context it is worth noting that the theoretical study predicts the companion product of CO from both the aziridine-like structure and/or from formyl isocyanate to be HNCO, isocyanic acid.

In any case, the only slightly positive temperature dependence of the total rate constant and the absence of any break in the Arrhenius plot give evidence that both the CO and CO₂ formation routes proceed without significant entrance barriers.

Conclusions

In this work, we have measured the rate coefficient k_5 of the HCCO + NO reaction, relative to the known coefficient of HCCO + O, over the temperature range of 290-670 K. The results lead to $k_5(T) = (1.0 \pm 0.3) \times 10^{-10} \text{ e}^{-(350 \pm 150)/(T/K)} \text{ cm}^3 \text{ molecule}^{-1}$ s⁻¹.

In addition, we have determined the product distribution at 700 K from direct measurements of the CO and CO₂ yields:

HCCO + NO → (CHNO)_{isomers} + CO
$$77 \pm 9\%$$

→ (CHN)_{isomers} + CO₂ $23 \pm 9\%$

The experimental results can be reconciled with the theoretical characterization of the [HC2NO2] potential energy surface18 only when a barrierless entrance pathway-as yet unidentified-to either the aziridine derivative or formyl isocyanate intermediates is assumed to exist. Both the magnitude of the rate constant and the nature of the products strongly indicate that the HCCO + NO reaction is highly relevant to NO chemistry in hydrocarbon combustion. This conclusion is based on the importance of the ketenyl radical in hydrocarbon flames, as noted earlier:^{3,7a,21} even in fuel-rich conditions, the key intermediate C_2H_2 is dominantly attacked by O atoms, yielding HCCO as major product.

In the context of reburn strategies, a recent modeling study by Smith et al.,²² adopting our k_5 expression, found the HCCO + NO reaction to have considerable impact. The study also concluded that of the common hydrocarbons C_2H_2 is the most efficient reburn fuel in reducing NO, owing largely to the sequence

$$C_2H_2 \xrightarrow{0} HCCO \xrightarrow{NO} HCNO \rightarrow HCN \xrightarrow{0} NCO \xrightarrow{H} NH \xrightarrow{NO} N_2$$

The theoretical prediction¹⁸ that HCCO + NO forms HNCO (isocyanic acid) rather than HCNO (fulminic acid) along with CO has important implications for reburn schemes. Indeed, HNCO—which is also essential in the RAPRENO_x process²—reacts with H to form CO plus NH₂;²³ in turn, the NH_2 radical can react with NO leading directly to N_2 :

$$HCCO \xrightarrow{NO} HNCO \xrightarrow{H} NH_2 \xrightarrow{NO} N_2$$

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