

Kinetics of the Reaction of NCO with Ethene and Oxygen
Over the Temperature Range 295-662K*

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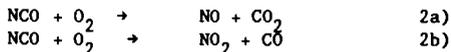
Introduction

The NCO radical is intimately connected with nitric oxide formation from fuel-bound nitrogen in combustion systems.^{1,2} In order to model nitrogen chemistry in combustion systems, it is essential to explore the possible chemical reactions that might enter into any extensive model of nitrogen chemistry in these systems. While little has been done toward understanding the detailed chemistry of the NCO radical with combustion species,¹⁻⁵ certain reactions can be anticipated to occur based upon analogous electrophilic radical/molecule reactions. One of these reactions is the reaction of NCO with ethene.



Unsaturated hydrocarbons are found extensively in combustion, with ethene being a major component after pyrolysis of larger fuels. This reaction was chosen to facilitate predictions of NCO radical reactions with unsaturated hydrocarbons and hence to understand more fully nitrogen chemistry in rich combustion systems. To the extent that this reaction occurs at combustion temperatures, it is a pathway to recycle reactive nitrogen radicals back into fuel-bound nitrogen i.e., HCN.

Other possible important reactions, if they occurred, are the exothermic reactions of NCO with oxygen.



Besides being of potential importance in combustion systems, these reactions could be important in atmospheric oxidation of HCN. An upper limit has been placed on the exothermic, although sterically restricted, reactions between NCO and oxygen.

In this paper current research that employs a laser photolysis/laser-induced fluorescence technique to measure absolute rate constants for the reaction of NCO radicals with ethene and oxygen over the

temperature range 295-662K is discussed. In addition, the pressure dependence of the reaction between NCO and ethene is explored at room temperature. The implications for combustion modeling will be addressed.

EXPERIMENTAL

The technique is essentially identical to that which was developed to study the products of the reaction of $O(^1P)$ with HCN.⁶ NCO radicals are produced from the excimer laser photolysis of HNCO that was introduced along with the reactant of interest in a flowing gas mixture of HNCO:Ar:reactant at total pressures (primarily argon) of 10-372 Torr. The NCO radicals result either directly from the photolysis of HNCO or, as suggested by Drozdowski et al.,⁷ from the rapid reaction of $NH(^1\Delta)$ with HNCO. (Recent experiments at 157 nm and 193 nm suggest that the latter is the dominant mechanism.⁸) Both 193 nm and 157 nm radiation are used to photolyze HNCO in order to check for interference due to photolysis products.

An argon ion pumped ring dye laser, operating with stilbene-3 dye at 416.8 nm (100mW), is used to pump the $A^2\Sigma(1,0,0) \leftarrow X^2\Pi(0,0,0)$ transition of NCO. The resulting fluorescence is monitored using an EMI 9789QA photomultiplier tube fitted with an interference filter at 438.5nm (FWHM=8.0nm) mounted at right angles to the crossed laser beams. The intersection of the detection system aperture and the laser-induced fluorescence radiation defined a fluorescence viewing zone at the center of the reaction vessel whose cross section was ~2cm in diameter. This region was well separated from the reaction vessel walls, minimizing wall losses of the NCO radicals. The reactor consisted of a quartz reaction vessel enclosed in a ceramic furnace that could be heated to temperatures as high as 1200K. The temperature of the furnace was monitored by Chromel/Alumel thermocouples mounted inside the reaction vessel, with the temperature of the vessel maintained to $\pm 5K$ over the entire temperature range.

The HNCO was synthesized according to the procedure of Okabe.⁹ Cyanuric acid was heated in an evacuable pyrex vessel to 400K. The HNCO generated was passed through a P_2O_5 and Ag_2O trap to remove the water, and HCN and was then condensed in a liquid nitrogen trap. The liquid was vacuum distilled using a dry-ice/acetone trap until constant vapor pressure (0.88 Torr) resulted. Argon was bubbled through the liquid and the resulting Ar/HNCO mixture was flowed to the reaction vessel. The flow rate was monitored by use of a rotameter. All other flows were monitored by the use of Tylan flow controllers that were calibrated prior to use.

The excimer laser intensity was varied by a factor of 2 using a purge tube situated between the excimer laser and the reaction vessel. Mixtures of nitrogen and oxygen were used to attenuate the 157 nm radiation, while nitrous oxide and air were used to attenuate radiation at 193 nm. All experiments were performed at a repetition rate of 0.3Hz. Signals were obtained by photon counting in conjunction with multichannel scaling. Decay curves of NCO radicals were accumulated from 25-500 pulses

depending on the signal strengths. NCO half-lives ranged from 2.43-200 msec, and the NCO radical concentrations were followed for at least three half-lives.

All experiments were carried out under slow-flow conditions so that the premixed reactant gas mixture could be replenished between laser pulses, thereby avoiding the accumulation of photolysis or reaction products. The partial pressure of HNCO was approximately 1.8-19 mTorr. The gases used had the following purity levels according to the manufacturer: Ar $\geq 99.995\%$; $C_2H_4 \geq 99.0\%$; $O_2 \geq 99.9995\%$.

RESULTS AND DISCUSSION

Over the entire temperature range 295-652K, and in the presence of excess reactant gas, pseudo-first order kinetics is observed, and the bimolecular rate constant is obtained using the expression:

$$\ln [NCO]_0 / [NCO]_t = \ln S_0 / S_t = (k_0 + k_i [\text{Reactant}])(t - t_0)$$

Here $[NCO]_0$ and $[NCO]_t$ are the concentrations of NCO radicals at times t_0 and t , respectively, S_0 and S_t are the corresponding fluorescence intensities, k_0 is the first order rate coefficient for removal of the NCO in the absence of added reactant, and k_i is the rate constant for reaction with the added reactant, i.e., ethene or oxygen.

The decay was analyzed following a ~ 1 ms delay after the excimer laser pulse to minimize interference from laser-induced emission from the silica vessel and to ensure that secondary reactions of other radical species formed during the photolysis event, such as $NH({}^1\Delta_7)$ would not interfere with the reaction of interest. In all experiments exponential decays were observed after the first millisecond supporting the contention that secondary reactions were not important. Also, at low pulse energies (≤ 1 mJ/pulse) no effect, within experimental uncertainty, due to laser intensity was observed with a factor of two change. (Without attenuating the excimer laser radiation the apparent rate was measured to be faster and decays were nonexponential.)

The data were analyzed by numerical least squares fitting of the decays. The measured decay rates were found to depend linearly on the concentration of added reactant for fixed total pressure and temperature. The absolute rate constants were determined by plotting the measured decay rate against reactant concentration and performing a least squares fit to obtain the slope, k_i .

Rate constants, k_1 , for the reaction of NCO with ethene were determined over the temperature range of 295-652K with the total pressure being varied from 10-372 Torr at 295K. Figures 1 and 2 show the plots of the data at 295K and higher temperatures, respectively, while Figure 3 shows a plot of the pressure dependence. Table I gives the rate constants determined for this reaction by least squares analysis over the entire temperature range.

Figure 4 shows an Arrhenius plot of the rate constants k_1 with the region from 295-447K being described by the following Arrhenius expression:

$$k_1 = 3.0 \times 10^{-12} e^{(230 \pm 300)/RT} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

where the error limit in the activation energy is the estimated overall error limit.

The pressure dependence observed at 295K (figure 3) is best explained by a Lindemann mechanism.



where complex^* is the complex formed by the terminal addition of NCO to ethene. The pressure dependent rate is given by the expression:

$$k_{bi} = k_a k_b [M] / (k_{-a} + k_b [M])$$

In the high pressure region where $k_b [M]$ is much greater than k_{-a} , $k_{bi} = k_a$, while in the low pressure region $k_{bi} = k_a (k_b [M] / k_{-a})$.

At temperatures greater than 447K a dramatic reduction in the bimolecular rate constant was observed. As seen in Figure 4 the reaction rate drops by greater than two orders of magnitude from 447K to 652K. This reduction in bimolecular rate constant apparently occurs due to the very rapid decomposition of the complex formed between NCO and ethene. Although such a dramatic reduction in reaction rate has been observed in the past for OH radical reactions, ¹⁰⁻¹⁴ nonexponential decays (after 1ms) were not apparent in these experiments. The absence of nonexponential decays suggest that the life time of the complex formed must be short in comparison to the experimental observation time. A proposed reaction mechanism whereby the thermalized adduct, [complex], begins to dissociate on a time scale that is comparable to the time frame of the experiments, analogous to the explanation of the effect observed for OH radical reaction with unsaturated hydrocarbons, ¹⁰⁻¹⁴ could explain the sharp drop in rate with increasing temperatures ($\geq 447\text{K}$), but in order to explain fully the essentially exponential decays observed in all of the experiments, competitive reactions that turn off at higher temperatures (or a different reaction mechanism that regenerates NCO radicals at higher temperatures) is required. Calculations are presently under way to address the possible alternate channels, such as ring closure to form the ethylene imine analog.

Using 193nm photolysis of H₂NCO, with a mixture of nitrous oxide and oxygen as a UV attenuator/filter, the reaction of NCO with oxygen was not observed to occur at room temperature and 372 Torr argon with

2.27×10^{16} molecule/cm³ of oxygen added. In addition no reaction was observed at 662K and 389 Torr when 2.4×10^{16} molecule/cm³ of oxygen was added. From these data the rate of reaction with oxygen was estimated to be less than 1×10^{-16} cm³molecule⁻¹s⁻¹ at 295 and less than 5×10^{-17} cm³molecule⁻¹s⁻¹ at 662K. These data suggest that under the conditions that exist in combustion environments or in the stratosphere, it is unlikely that the reaction of NCO with oxygen will be important. As suggested by Cicerone and Zellner¹³, the primary fate of NCO in the atmosphere is most likely photolysis at wavelengths less than 300 nm.

CONCLUSIONS

At low temperatures the NCO radical will react with ethene to form a complex. At temperatures greater than 450K a marked decrease in the rate of reaction occurs until finally at 650K the reaction has decreased by two orders of magnitude. This effect suggests that the reaction with ethene, or, by inference, other unsaturated hydrocarbons, will not serve to recycle the NCO radical in combustion environments.

At the temperatures of this study NCO radicals do not react with molecular oxygen. The reaction of NCO with oxygen should be unimportant in combustion or atmospheric systems.

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Table I. Rate constants, k_1 , for the reaction of NCO radicals with ethene. The indicated error limits are the estimated overall error limits; they include the least squares standard deviations (2.0-15%), as well as the estimated accuracy limits of other parameters such as pressure and reactant concentrations.

Temperature (K)	Total Pressure (Torr)	$k_1 \times 10^{12}$ (cm ³ molecule ⁻¹ s ⁻¹)
295	10.5	3.37 ± 0.57
295	25.0	3.78 ± 0.38
295	53.3	4.37 ± 0.44
296	102.0	4.39 ± 0.44
296	204.0	4.58 ± 0.46
295	372.0	4.69 ± 0.47
330	198.0	4.00 ± 0.40
381	203.0	3.99 ± 0.40
447	200.0	3.88 ± 0.39
487	202.0	2.56 ± 0.64
535	201.0	1.30 ± 0.26
585	372.0	0.112 ± 0.02
652	372.0	0.027 ± 0.005

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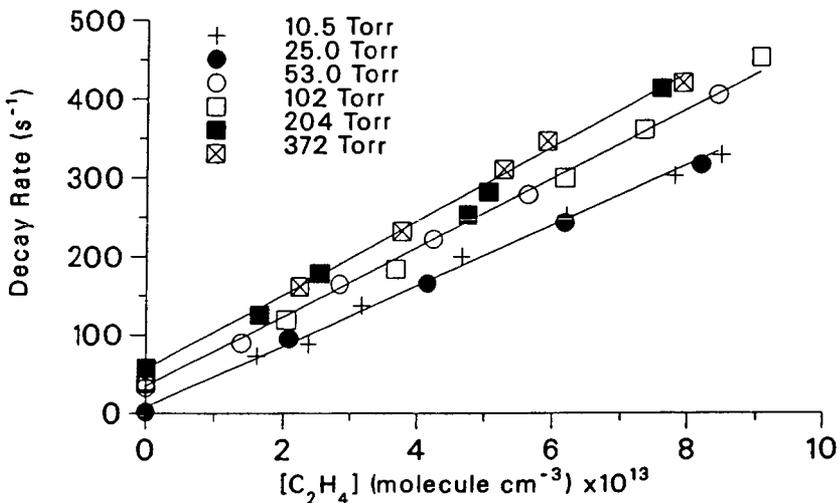


Figure 1. Plots of the decay rate against ethene concentration for the reaction on NCO with ethene at 295K. The solid lines represent best fit to data at 25 Torr, 53 Torr and 372 Torr.

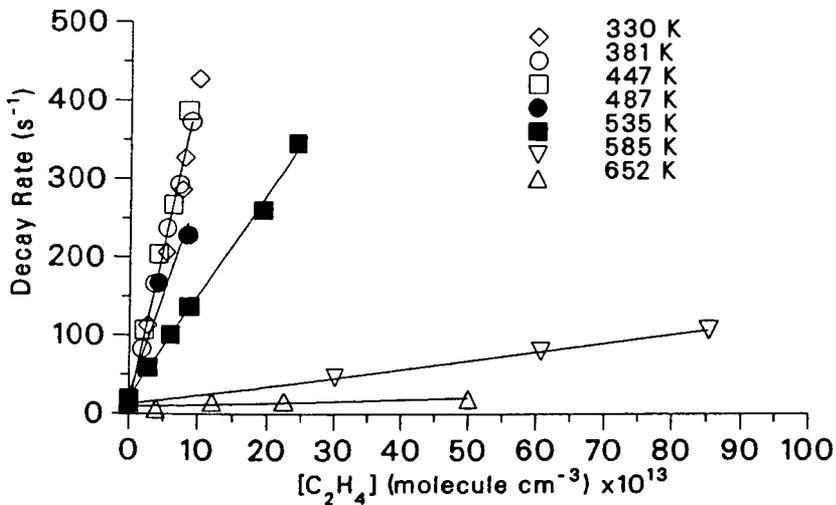


Figure 2. Plots of the decay rate against ethene concentration.

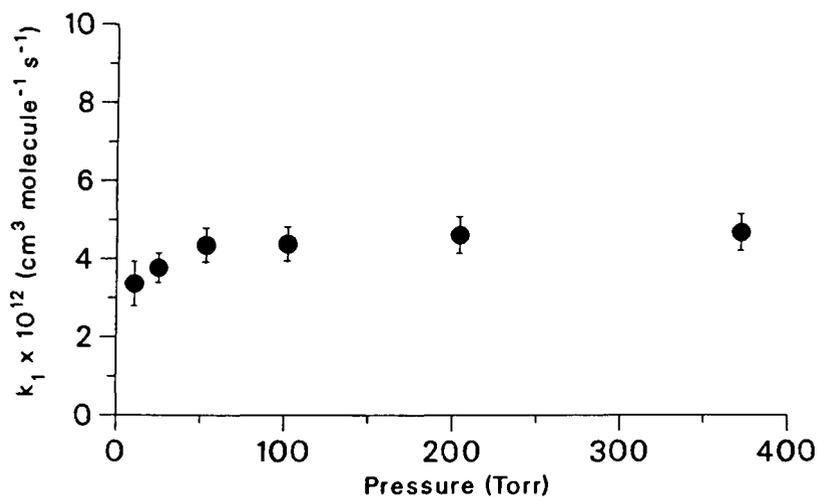


Figure 3. Plot of the rate constant versus pressure at room temperature.

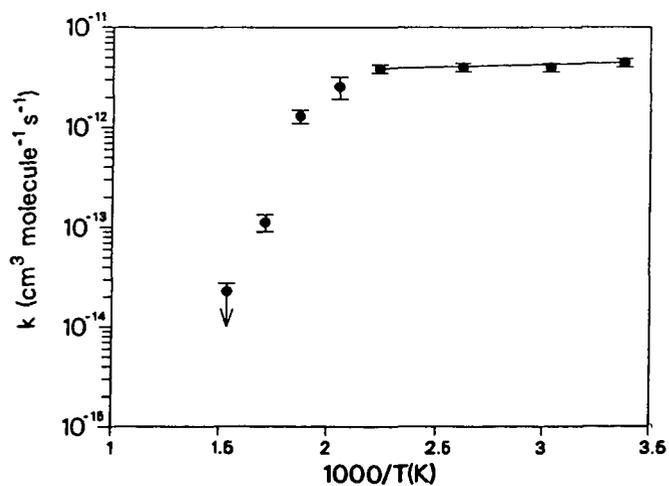


Figure 4. Arrhenius plot of $\log k_1$ for the reaction of NCO with ethene against $1000/T$ (K). The solid line is the least squares fit to the data for the temperature range 295-447.