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Kinetic Investigation of the Reactions of NCO Radicals with Alkanes in the Temperature Range 294 to 1113 K

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Absolute rate coefficients for the reaction of NCO radicals with methane (k_1), ethane (k_2), and propane (k_3) were measured as a function of temperature in a heatable quartz reactor by means of the laser photolysis/laser-induced fluorescence (LP/LIF) pump-probe technique. NCO radicals were produced by the fast precursor reaction $NH(a^1\Delta) + HNCO \rightarrow NH_2 + NCO$, following the 193-nm photolysis of isocyanic acid. The measured rate coefficients can be described by the following expressions:

$$k_1(512 < T < 1113\ K) = 10^{12.99 \pm 0.12} \times \exp(-34.0 \pm 1.8\ kJ\ mol^{-1}/RT)\ cm^3\ mol^{-1}\ s^{-1}, \tag{1}$$

$$k_2(296 < T < 922\ K) = 10^{8.21} \times (T/298\ K)^{(6.89 \pm 0.02)} \times \exp(12.2 \pm 0.5\ kJ\ mol^{-1}/RT)\ cm^3\ mol^{-1}\ s^{-1}, \tag{2}$$

$$k_3(300 < T < 849\ K) = 10^{11.49} \times (T/298\ K)^{(2.15 \pm 0.02)} \times \exp(-1.8 \pm 0.4\ kJ\ mol^{-1}/RT)\ cm^3\ mol^{-1}\ s^{-1}. \tag{3}$$

A comparison with the corresponding reactions of CN, Cl, and OH radicals with alkanes suggests that all these title reactions also proceed predominantly via a hydrogen atom abstraction mechanism to form HNCO.

INTRODUCTION

The NCO radical is an important intermediate species in a variety of practical combustion processes. NCO arises from fuel-bound nitrogen via oxidation of species containing CN bonds, and its subsequent reactions play a key role in the fuel nitrogen conversion [1]. The reaction of NCO with NO has been suggested to be primarily responsible for NO removal in the RAPRENO$_x$ process [2, 3]. Moreover, NCO precursors, such as HCN and HNCO, are products of NO reduction in the presence of hydrocarbons [4, 5]. The reaction of NCO with NO has been investigated thoroughly [6–13]. Atakan et al. [9] measured reaction rates for NCO + NO in the temperature range 294–1260 K. The modified Arrhenius expression derived in this study was confirmed by shock tube studies of Mertens et al. [12], carried out in the temperature range 2380–2660 K. Rates of the reactions of NCO with O, H_2 and C_2H_4, as well as an upper limit for the reaction NCO + O_2, were determined [6, 9, 14, 15].

In a recent investigation the kinetics of NCO + hydrocarbon reactions were investigated by Park and Hershberger [16] and room temperature rate constants were measured for the reactions of NCO radicals with CH_4, C_2H_6, C_3H_8, n-C_4H_{10}, n-C_5H_{12}, C_2H_2, and C_2H_4, respectively. Hydrogen abstraction leading to HNCO was observed to be a major product channel for the reactions with alkanes and C_2H_2 [16]. However, up to now no rate constants have been available for the reactions of NCO with saturated hydrocarbons in the temperature range relevant to combustion. In order to fill this gap, in the present study rate coefficients were measured for the reactions of NCO with methane (1), ethane (2), and propane (3) at elevated temperatures. The data will allow the inclusion of these reactions in kinetic models of processes, such as reburning and hydrocarbon-broadened selective non-catalytic reduction of NO (SNCR) [17, 18].

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EXPERIMENTAL

All measurements were carried out in a heatable quartz reactor, depicted schematically in Fig. 1. Photolysis of HNCO at 193 nm was employed to generate NCO radicals. The gas mixture, consisting of HNCO (diluted in N_2) and the reactants, was introduced into the reactor via inlet I_1 (see Fig. 1). The reactor is fitted in a steel tube to provide a homogeneous temperature profile. The main part of the steel tube is heated by a furnace. In the region near the side arms, temperature gradients were avoided by using additional heating wires. The temperature was measured by a retractable nisil/nicrosil (Philips) thermocouple near the photolysis zone. In addition, measured temperatures were checked by measuring the rotational temperature of CN radicals in the vibrational ground state (generated by C_2N_2 photodissociation at 193 nm). Good agreement between the temperatures measured with the two different methods was found [9].

The photolysis and the probe laser beams propagated in opposite directions through the side arms of the reactor. HNCO was photodissociated at 193 nm using an ArF excimer laser (Lambda LPX 205). A XeCl excimer laser (Lambda EMG 201 MSC) pumped dye laser (Lambda FL 2002 EC), operated with QUI dye, was used to excite the Q_1 bandhead of the $^2\Pi(a)(0,0^1,0) \rightarrow {}^2\Sigma^+(0,0^0,1)$ band of NCO at 397.818 nm. The dye laser beam was expanded with a telescope and attenuated until the measured fluorescence signal showed a linear dependence on the probe laser intensity. The emitted red-shifted fluorescence was collected by a lens perpendicular to the laser beam's direction and focused upon the cathode of a photomultiplier (EMI 9781), equipped with a combination of filters (Schott GG 420, UG 5, KG 2) which served as a bandpass filter between 420 and 530 nm. The LIF signal was measured by a Boxcar integrator (SR 250) and transferred via an analog-to-digital converter (SR 235) to a microcomputer (Hewlett Packard series 9000, model 320) which was also used to control the timing of the experiment by means of a delay generator (SR DG 535). The fluorescence signal was normalized to both laser intensities, which were measured by photodiodes.

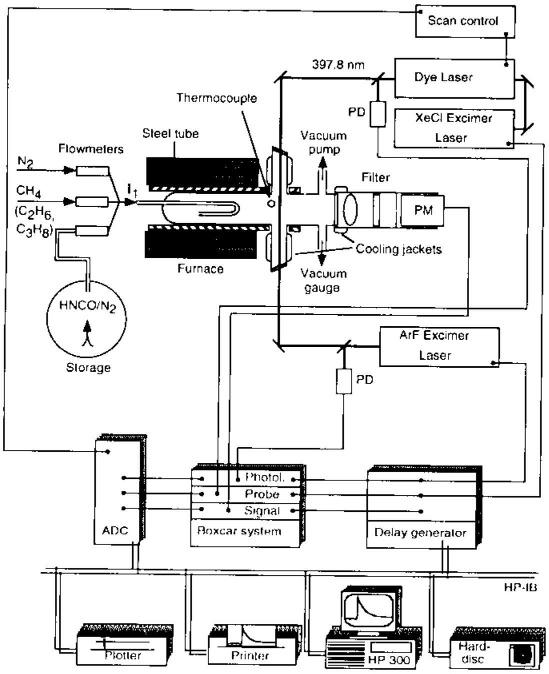

Fig. 1. Schematical description of the experimental set-up of the laser photolysis laser induced fluorescence apparatus.

A mixture of HNCO and N_2 was prepared in a 10-L storage vessel by evaporating 20 torr of HNCO and adding 740 torr N_2. All gas flows were regulated by calibrated mass flow controllers (Tylan). The total pressure in the reactor was measured by a MKS Baratron. Typical partial pressures of the gases used are listed in Tables 1–3. The gases used had the following purities: $N_2 > 99.996\%$, CH_4, C_2H_6, $C_3H_8 > 99.998\%$ (all Messer Griesheim).

HNCO was synthesized by vacuum depolymerization of cyanuric acid following the procedure described by Linhard [19]. Cyanuric acid, purified by double recrystallization from water, was dryed in vacuo at 200°C. It was volatilized at 400°C and the gas stream was passed through a hotter tube furnace at 700°C. The transport of the sublimed material was aided by a slight Helium gas flow. The HNCO generated was condensed in a liquid nitrogen trap and purified by trap to trap distillation from $-30°$ to $-80°C$, using traps charged with Ag_2O and P_4O_{10} in order to remove HCN and water, respectively.

TABLE 1

Reaction Conditions and Measured Rate Constants with Methane as Reactant with NCO

T	P	$[N_2]_{\text{min-max}}$	[HNCO]	$[CH_4]_{\text{min-max}}$	$k'_{\text{min-max}}$	k_D	k_1
(K)	(torr)	(10^{-8} mol cm^{-3})			(10^3 s^{-1})	(10^3 s^{-1})	(10^{10} cm^3 mol^{-1} s^{-1})
512	43	81–122	0.6	12–53	1.58–3.34	1.3 ± 0.2	0.395 ± 0.088
687	50	85–111	0.4	4.3–30.3	2.25–9.75	1.5 ± 0.5	2.50 ± 0.56
754	59	93–120	0.7	3.8–31.0	3.24–15.1	2.2 ± 0.5	3.49 ± 0.44
800	55	95–107	0.4	1.5–14.0	3.34–9.50	3.1 ± 0.3	4.69 ± 0.76
850	42	52–57	0.3	3.0–26.0	4.16–21.2	1.2 ± 1.0	8.74 ± 1.64
928	52	71–85	0.3	3.3–18.0	5.10–20.6	1.3 ± 0.6	10.3 ± 1.1
982	55	80–87	0.3	1.8–8.2	4.60–16.0	1.9 ± 0.3	19.9 ± 3.4
1057	45	59–67	0.3	0.92–8.8	3.77–19.7	2.9 ± 1.3	19.4 ± 5.8
1113	43	58–60	0.3	0.87–3.4	3.43–12.1	2.8 ± 0.7	30.4 ± 5.4

EXPERIMENTAL RESULTS AND DISCUSSION

HNCO photolysis at 193 nm yields predominantly NH($a^1\Delta$) and CO [20, 21]. Recently, a value of 0.05 was reported for the branching ratio for the H + NCO product channel [18]. Thus, NCO is produced mainly via the reaction:

$$NH(a^1\Delta) + HNCO \rightarrow NH_2 + NCO. \qquad (4)$$

Reaction 4 is known to be very fast [22–24]. With the value of the rate constant [24] of $k_4 = 3.28 \times 10^{13}$ cm^3 mol^{-1} s^{-1}, reaction 4 proceeds on a microsecond timescale at the HNCO partial pressures typically employed in the present study, as can be seen in Fig. 2, which shows the time profile of the NCO signal following the photolysis laser pulse. By way of contrast, with our experimental conditions the reactions under study occur on a timescale of several 100 μs. Thus, the rate constants can be derived from the decay part of the NCO signal versus time profiles (as shown in Fig. 3) using the following single exponential expression

$$I(t)/I_{\max} = [NCO](t)/[NCO]_{\max} = \exp(-k't), \qquad (5)$$

where I denotes the fluorescence intensity and $I_{\max}$ is the maximum of the fluorescence intensity. Possible side reactions that can result in

TABLE 2

Rate Coefficients Measured for Reaction of NCO with Ethane

T	p	$[N_2]_{\text{min-max}}$	[HNCO]	$[C_2H_6]_{\text{min-max}}$	$k'_{\text{min-max}}$	k_D	k_2
(K)	(torr)	(10^{-8} mol cm^{-3})			(10^3 s^{-1})	(10^3 s^{-1})	(10^{11} cm^3 mol^{-1} s^{-1})
296	44	165–228	0.9	7.5–73	4.1–20.4	2.0 ± 0.9	0.238 ± 0.038
368	44	134–183	0.7	5.8–57	2.36–14.4	1.4 ± 0.5	0.290 ± 0.032
416	45	118–167	0.6	4.5–52	2.9–33.0	3.2 ± 0.9	0.599 ± 0.052
464	53	128–175	0.7	6.0–53	8.54–55.5	1.9 ± 2.2	0.979 ± 0.159
513	43	107–129	0.5	3.5–26	5.13–33.6	0.9 ± 0.6	1.19 ± 0.07
592	44	98–118	0.4	2.4–22	4.76–47.3	1.3 ± 0.8	2.09 ± 0.12
659	60	138–143	0.5	0.73–6.5	6.41–28.2	4.6 ± 1.4	3.51 ± 0.76
749	68	128–140	0.6	4.1–16	13.2–69.2	−0.9 ± 2.1	6.70 ± 2.08
922	72	120–123	0.5	0.64–3.4	7.42–46.9	0.8 ± 3.4	19.3 ± 4.9

TABLE 3

Measured Rate Constants for NCO + Propane

T (K)	p (torr)	$[N_2]_{min\text{-}max}$	[HNCO]	$[C_3H_8]_{min\text{-}max}$	$k'_{min\text{-}max}$ (10^3 s^{-1})	k_D (10^3 s^{-1})	k_3 (10^{11} cm^3 mol^{-1} s^{-1})
		(10^{-8} mol cm^{-3})					
300	47	222–245	0.7	3.2–26	1.7–40.8	0.9 ± 2.2	1.6 ± 0.3
464	48	136–162	0.6	2.1–20	17.2–96.6	−0.3 ± 4.2	4.7 ± 0.8
656	48	104–114	0.7	1.5–12	27.1–173	−0.6 ± 7.5	13.5 ± 2.2
849	47	85–88	0.7	0.16–2.9	6.0–66.6	2.6 ± 1.1	21.6 ± 1.4

the formation or decay of NCO are Eqs. 6–11.

$$NH_2 + HNCO \rightarrow NH_3 + NCO, \qquad (6)$$

$$H + HNCO \rightarrow H_2 + NCO, \qquad (7)$$

$$NH_2 + RH \rightarrow NH_3 + R, \qquad (8)$$

$$R = CH_3, C_2H_5, C_3H_7,$$

$$NH_3 + NCO \rightarrow \text{products}, \qquad (9)$$

$$R + NCO \rightarrow \text{products}, \qquad (10)$$

$$R + HNCO \rightarrow RH + NCO. \qquad (11)$$

For reaction 6, which could produce NCO, rate constant values are not available in the temperature range of our study. In a recent shock tube study [25], reaction 6 has been investigated in the temperature range from 2340 up to 2680 K, and an estimate for the temperature dependence of k_6 was reported.

$$k_6 = 1.0 \times 10^{12} \times \exp(-3500\ K/T)\ \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}$$

Using this expression, we found (6) to be too slow to interfere either directly or via (9) with the reactions under study, even in case of the slowest title reaction, (1), and at the lowest alkane concentrations. The same holds for reaction (7), and also (8)—followed by (9) and (10)—for which rate coefficients are reported in the literature [26–29]. Due to the high endothermicity of (11) [30], a significant production of NCO via these reactions can also be ruled out at the temperatures typically used in our studies.

In order to investigate the influence of vibrationally excited NCO which could possible be formed in (4), on the measured rate constants for (1), (2), and (3), the time history of NCO(0, 0, 0) formation in the absence of reactants was investigated in detail. Figure 2 shows the time history of NCO(0, 0, 0) formation in the absence of reactants during the first 10 μs. No noticeable rise in the vibrational ground state NCO concentration could be observed at delay times up to 200 μs. Thus effects of

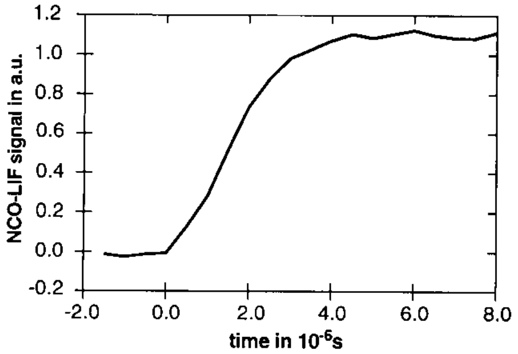

Fig. 2. NCO(0, 0, 0) time history following the dissociation of HNCO in the absence of alkanes. Total pressure ($HNCO/N_2$) p_{tot} = 28 torr; HNCO partial pressure p_{HNCO} = 370 mTorr.

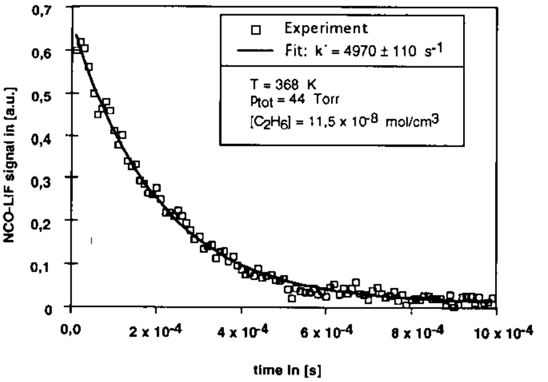

Fig. 3. NCO fluorescence delay scan. The pseudo-first-order rate constants (k') was determined using a least-squares procedure.

vibrational relaxation on the NCO decay profile can be ruled out. Moreover, under all experimental conditions single exponential decay of NCO was clearly observed.

The least-squares analysis of the NCO profiles yields $k' = k'' + k_D$, with the pseudo-first order rate coefficient k'', and a constant, k_D, accounting for additional loss processes. The measured decay rates were found to depend linearly on reactant concentrations and bimolecular rate constants were derived from the slope of plots of k' versus reactant concentration.

Reaction (1) was studied at 11 different temperatures between room temperature and 1113 K. At 296 K and 368 K, reaction (1) was too slow to distinguish between reaction and diffusion loss. Thus at these temperatures no rate constants could be determined. However, reaction (1) shows a strong temperature dependence, with its rate constant increasing by a factor of 50 between 512 K and 1113 K. The temperature dependent rate constants together with the experimental conditions are listed in Table 1. In Fig. 4, the pseudo-first-order rate constants (k') are plotted versus methane concentration for different temperatures. For clarity, not all of the k' versus $[CH_4]$ plots have been included. No significant deviation from Arrhenius behavior was found between 512 and 1113 K, and the data could be fitted by the following, two-parameter expression:

$$k_1(512 < T < 1113\ K) = 10^{12.99 \pm 0.12} \times \exp(-34.0 \pm 1.8\ kJ\ mol^{-1}/RT) \times cm^3\ mol^{-1}\ s^{-1}.$$

The rate coefficient of reaction 2 with ethane as reactant was determined at 9 different temperatures between 296 and 922 K. The results are given in Table 2, and a selection of the k' plots is depicted in Fig. 5. An increase in the rate coefficient of (2) by about two orders of magnitude was found. In contrast to reaction (1), the Arrhenius plot of (2) is markedly curved, and the data can be represented by a three parameter expression.

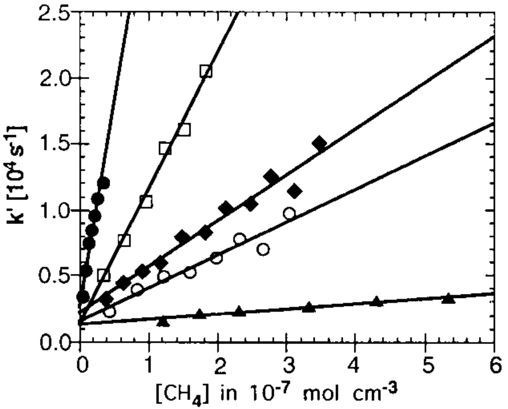

Fig. 4. Plots of pseudo-first-order rate constants (k') for reaction (1) at different temperatures.

$$k_2(296 < T < 922\ K) = 10^{8.21} \times (T/298\ K)^{(6.89 \pm 0.02)} \times \exp(12.2 \pm 0.5\ kJ\ mol^{-1}/RT) \times cm^3\ mol^{-1}\ s^{-1}.$$

Reaction 3 was investigated at four different temperatures between 300 and 849 K. The rate coefficients were found to increase by about one order of magnitude (see Table 3 and Fig. 6). The data can be described by the three

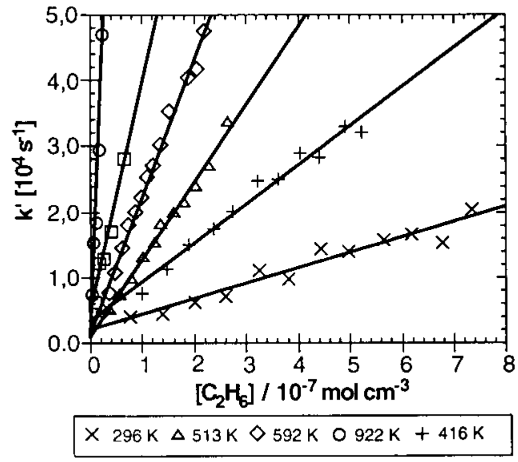

Fig. 5. Plots of pseudo-first-order rate constants (k') for reaction (2) at different temperatures.

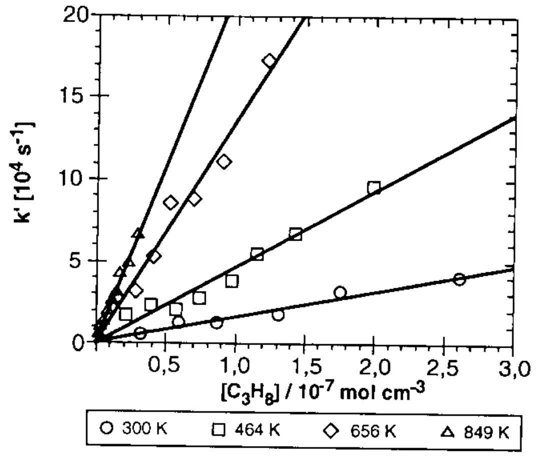

Fig. 6. Plots of pseudo-first-order rate constants (k') for reaction (3) at different temperatures.

parameter expression:

$$k_3(300 < T < 849\ \text{K}) = 10^{11.49} \times (T/298\ K)^{(2.15 \pm 0.02)} \times \exp(-1.8 \pm 0.4\ \text{kJ mol}^{-1}/RT) \times \text{cm}^3\ \text{mol}^{-1}\ \text{s}^{-1}.$$

The expressions given above were derived by means of a least-squares procedure in order to obtain the most accurate expressions for the interpolation of our experimental data, without attributing any physical meaning to the parameters [31].

In Fig. 7, the Arrhenius plots of the three title reactions are shown. The quoted errors in Tables 1–3 are 95% confidence intervals. For reactions (1) and (3), the values of our room temperature rate constants are in good agreement with previous values [16]. In the case of reaction (2), the value reported in Ref. 16 is about a factor of 1.8 higher than our value. To the best of our knowledge in the present study the reactions of NCO radicals with saturated hydrocarbons were investigated for the first time at elevated temperatures.

It is instructive to make a comparison with the related reactions of the CN radical, since both CN and NCO radicals are similar to halogens in some of their chemical properties, hence the name pseudo-halogens. The reaction of CN radicals with hydrocarbons have been investigated extensively, and the reactions with saturated hydrocarbons are supposed to be H atom abstraction reactions leading to HCN or HNC as products [32–40]. Compared with CN, the rate constants of the NCO + alkane reactions are lower by about 2–3 orders of magnitude, thus being closer to the corresponding rate constants of the OH + alkane reactions. An enhancement of the reaction rate with increasing chain length of the reactant occurs, by analogy with the CN reactions. It is most pronounced in going from methane to ethane. This enhancement, which was also found in the H-atom abstraction reactions of Cl atoms and OH radicals [41], corresponds to the decline in the ionization potential of the alkanes. In the temperature-dependent investigations of the CN + alkane reactions [33–36] the strongest temperature dependence was found for the CN + methane reaction, whereas only a slight temperature dependence for the CN + propane reaction was found [9, 10]. As can be seen from Fig. 6, a similar trend in the rate constants is apparent for the corresponding NCO reactions. Therefore the increase in the measured reaction rate with increasing chain length of the alkanes can be explained by a hydrogen abstraction mechanism (leading to HNCO as the main product [16]) as observed in the corresponding reactions with CN, and OH radicals as well as Cl atoms.

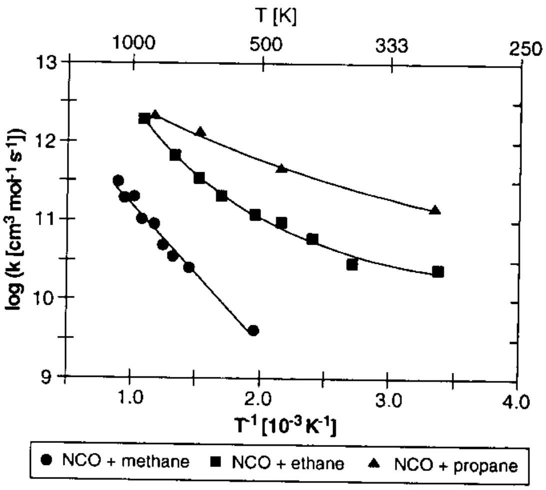

Fig. 7. Arrhenius plots for the reactions of NCO radicals with alkanes.

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REFERENCES

1. Miller, J. A., and Bowman, C. T., *Prog. Ener. Combust. Sci.* 15:287–338 (1989).
2. Perry, R. A., and Siebers, D. L., *Nature* 324:657–658 (1986).
3. Miller, J. A., and Bowman, C. T., *Int. J. Chem. Kinet.* 23:289–313 (1991).
4. Nelson, P. F., and Haynes, B. S., Joint meeting of the Australian and New Zealand Combustion Symposium, November 1993.
5. Muris, S., PhD thesis, University of Heidelberg, 1993.
6. Perry, R. A., *J. Chem. Phys.* 82:5485–5488 (1985).
7. Cookson, J. L., Hancock, G., and McKendrick, K. G., *Ber. Bunsenges. Phys. Chem.* 89:335–336 (1985).
8. Hancock, G., and McKendrick, K. G., *Chem. Phys. Lett.* 127:125–129 (1986).
9. Atakan, B., and Wolfrum, J., *Chem. Phys. Lett.* 178:157–162 (1991).
10. Cooper, W. F., and Hershberger, J. F., *J. Phys. Chem.* 96:771–775 (1992).
11. Becker, K. H., Kurtenbach, R., and Wiesen, P., *Chem. Phys. Lett.* 198:424–428 (1992).
12. Mertens, J. D., Dean, A. J., Hanson, R. K., and Bowman, C. T., *Twenty-Fourth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1992, pp. 701–710.
13. Cooper, W. F., Park, J. and Hershberger, J. F., *J. Phys. Chem.* 97:3283–3290 (1993).
14. Louge, M. Y., and Hanson, R. K., *Twentieth Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1984, pp. 665–672.
15. Perry, R. A., *Twenty-First Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1986, pp. 913–918.
16. Park, J. and Hershberger, J. F., *Chem. Phys. Lett.* 218:537–543 (1994).
17. Hemberger, R. S., Murris, S., Pleban, K.-U., and Wolfrum, J., *Twenty-Fifth Symposium (International) on Combustion* (1994) (to be presented).
18. Nelson, P. F., and Haynes, B. S., "Hydrocarbon-NO_x Interactions at Low Temperatures-1. Conversion of NO to NO_2 promoted by propane and the formation of HNCO", preprint (1994).
19. Linhard, M., *Z. Anorg. Chem.* 236:200–209 (1938).
20. Spiglanin, T. A., Perry, R. A., and Chandler, D. W., *J. Phys. Chem.* 90:6184–6189 (1990).
21. Whikun, Y., and Bersohn, R., *Chem. Phys. Lett.* 206:365–368 (1993).
22. Drozdoski, W. S., Baronavski, A. P., and McDonald, J. R., *Chem. Phys. Lett.* 64:421–425, (1979).
23. Bower, R. D., Jacoby, M. T. and Blauer, J. A., *J. Chem. Phys.* 86:1954–1956 (1987).
24. Bohn, B. and Stuhl, F., *J. Phys. Chem.* 97:7234–7238 (1993).
25. Mertens, J. D., Kohse-Hoinghaus, K., Hanson, R. K., and Bowman, C. T., *Int. J. Chem. Kinet.* 23:655–668 (1991).
26. Demissy, M., and Leclaux, R., *J. Am. Chem. Soc.* 102:2897–2902 (1980).
27. Baulch, D. L., Cobos, C. J., Cox, R. A., Esser, C., Frank, P., Just, Th., Kerr, J. A., Pilling, M. J., Troe, J., Walker, R. W. and Warnatz, J., *J. Phys. Chem. Ref. Data* 21 (1992).
28. Hack, W., Kurzke, H., Rouveirolles, P. and Wagner, H. Gg., *Twenty-First Symposium (International) on Combustion*, The Combustion Institute, Pittsburgh, 1986, pp. 905–911.
29. Ehbrecht, J., Hack, W., Rouveirolles, P. and Wagner, H. Gg., *Ber. Bunsenges. Phys. Chem.* 91:700–708 (1987).
30. Melius, C., BAC-MP4 Heats of Formation and Free Energies, Sandia National Laboratories, Livermore, CA, U.S.A., 1990.
31. Héberger, K., Kemény, S. and Vidóczy, T., *Int. J. Chem. Kinet.* 19:171–181 (1987).
32. Lichtin, D. A., and Lin, M. C., *Chem. Phys.* 96:473–482 (1985).
33. Sayah, N., Li, X., Caballero, J. F., and Jackson, W. M., *J. Photochem. Photobiol. A* 45:177–194 (1988).
34. Schacke, H., Wagner, H. Gg., and Wolfrum, J., *Ber. Bunsenges. Phys. Chem.* 81:670–676 (1977).
35. Anastasi, C., and Hancock, D. U., *J. Chem. Soc. Farad. Trans. II* 84:9–15 (1988).
36. Bullock, G. E., and Cooper, R., *J. Chem. Soc. Farad. Trans. I* 68:2185–2190 (1972).
37. Hess, W. P., Durant, J., and Tully, F. P., *J. Phys. Chem.* 93:6402–6407 (1989).
38. Atakan, B., and Wolfrum, J., *Chem. Phys. Lett.* 186:547–552 (1991).
39. Copeland, L. R., Mohammad, M., Zahedi, M., Volman, D. H., and Jackson, W. M., *J. Chem. Phys.* 96:5817–5826 (1992).
40. Yang, D. L., Yu, T., Wang, N. S., and Lin, M. C., *Chem. Phys.* 160:307–315 (1992).
41. Atkinson, R., Baulch, D. L., Cox, R. A., Hampson, R. F., Jr., Kerr, J. A., and Troe, J., *J. Phys. Chem. Ref. Data* 18 (1989).

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COMMENTS

P. Wiesen, University of Wuppertal, Germany. Why did you choose an indirect route for the formation of NCO radicals by the reaction of NH radicals with HNCO instead of photolyzing ClNCO or BrNCO, since it is known that these species are very efficient precursors for NCO radicals.

Author's Reply. In contrast to the photodissociation of ClNCO and BrNCO, the photodissociation of HNCO at 193 nm has been characterized in detail [1–3]. In addition, we found HNCO to be thermally stable over the temperature range (294 K $< T <$ 1113 K) of our studies.

REFERENCES

1. Drozdoski, W. S., Baronavski, A. P., and McDonald, J. R., *Chem. Phys. Lett.* 64: 421–425 (1979).
2. Spiglanin, T. A., Perry, R. A., and Chandler, D. W., *J. Phys. Chem.* 90: 6184–6189 (1986).
3. Bersohn, R., and Yi, W., *Chem. Phys. Lett.* 206: 365–368 (1993).