

Kinetic investigation of NCO radicals reacting with selected hydrocarbons

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Bimolecular rate coefficients for the reactions of isocyanate radicals (NCO) with ethane (C₂H₆), allene (C₃H₄), propene (C₃H₆), but-1-ene (C₄H₈) and but-1-yne (C₄H₆) were measured in argon as carrier gas. NCO radicals have been formed using excimer laser photolysis of chlorine isocyanate (ClNCO) and were detected in their electronic ground state, $\tilde{X}^2\Pi$, by laser-induced fluorescence. The NCO + C₂H₆ reaction was investigated at 20 Torr total pressure in the temperature range 297–899 K. The reaction exhibits a positive temperature dependence which is well described by the following modified Arrhenius equation:

$$k_{\text{NCO}+\text{C}_2\text{H}_6}(T) = (6.2^{+3.8}_{-3.7}) \times 10^{-14} (T/298)^{(3.27 \pm 0.84)} \exp[-(2.5^{+3.4}_{-2.3})/RT] \text{ cm}^3 \text{ s}^{-1}$$

In addition, measurements carried out at 651 K in the pressure range 5–528 Torr showed no pressure dependence, which supports the view that the NCO + C₂H₆ reaction proceeds as a simple H atom abstraction. For the reaction of NCO radicals with allene (C₃H₄), propene (C₃H₆), but-1-ene (C₄H₈) and but-1-yne (C₄H₆) bimolecular rate coefficients were determined at room temperature and at 20 Torr total pressure. Additionally, the reactions of NCO with C₃H₄ and C₄H₆ were studied at different total pressures. For both reactions, no pressure dependence was observed. The following rate coefficients were obtained at 298 K (in units of 10⁻¹¹ cm³ s⁻¹): $k_{\text{NCO}+\text{C}_3\text{H}_4} = (1.39 \pm 0.18)$, $k_{\text{NCO}+\text{C}_3\text{H}_6} = (4.29 \pm 0.20)$, $k_{\text{NCO}+\text{C}_4\text{H}_8} = (6.18 \pm 0.46)$ and $k_{\text{NCO}+\text{C}_4\text{H}_6} = (1.41 \pm 0.14)$. A correlation between the measured bimolecular rate coefficients of the NCO reactions with unsaturated hydrocarbons and their ionisation potentials was established.

1. Introduction

The emission of nitrogen oxides is a major problem concerned with the combustion of fossil fuels. NCO radicals are important intermediates in combustion processes leading to the formation of NO, in particular in the conversion of fuel nitrogen into nitrogen oxides and in the so called “prompt” NO formation.^{1–3} The main reaction pathways leading either directly or indirectly, *e.g.*, via NH radicals, to the formation of NO are the fast reactions of NCO radicals with O and H atoms:^{4,5}



In addition, the NCO radical is a key intermediate in NO_x reduction processes such as the RapReNO_x process.⁶ In these processes NCO radicals react rapidly with NO with a rate coefficient of the order of magnitude of about 10⁻¹¹ cm³ s⁻¹.⁷

This study continues the work of our laboratory on kinetic investigations of NCO radicals reacting with unsaturated hydrocarbons,^{8,9} all of which are commonly observed in combustion processes.¹⁰ Prior to the work reported here rate coefficients were only available for the reactions of NCO radicals with a limited number of hydrocarbons such as C₂H₄,⁸ C₂H₂,⁹ C₃H₆,¹¹ and C₂H₆.^{11,12}

In this study, the NCO + C₂H₆ reaction was investigated at 20 Torr total pressure in the temperature range 297–899 K and at 651 K in the pressure range 5–528 Torr using a pulsed excimer laser photolysis (ELP)–laser induced fluorescence (LIF) technique. In addition, the reactions of NCO radicals

with C₃H₄, C₃H₆, C₄H₈ and C₄H₆ were studied at room temperature and different total pressures for the first time.

The aim of the determination of rate parameters for NCO radical reactions with these small hydrocarbons was twofold. First, it should be examined whether the rates of these reactions can compete with the fast reactions of NCO radicals with NO or O and H atoms in combustion processes. Second, the correlation between the rate coefficients of the NCO reactions investigated and the ionisation potential of the reacting hydrocarbons, which was proposed by Wategaonkar and Setser¹¹ for the first time, was examined in order to check whether this correlation can be used for an estimation of reaction rate coefficients for NCO reactions with hydrocarbons.

2. Experimental

Bimolecular rate coefficients were obtained under pseudo-first-order conditions using a standard photolysis–probe laser technique. The experimental set-up used was similar to that employed previously in our laboratory.⁷

NCO radicals were generated pulsewise by excimer laser (Lambda EMG 102) photolysis of ClNCO–Ar mixtures at 248 nm. The typical pulse energy of the photolysis laser was 100 mJ. The relative NCO radical concentration was measured as a function of the reaction time in the range 10 μs–20 ms by LIF from the integrated intensity of the Q₁ branch of the $\tilde{A}^2\Sigma^+(000) \rightarrow \tilde{X}^2\Pi(000)$ transition at 438.6 nm. The probe laser was a Lambda Physik system comprising a FL 3001 dye laser with an EMG 102 excimer laser. The dye laser was operated with Coumarine 120 (Radiant Dyes) in methanol, yielding typical pulse energies of about 2 mJ. Both laser systems

were operated at a repetition rate of 10 Hz. The time delay between the photolysis and the probe laser was varied from zero to several milliseconds using a digital delay generator (BNC 7010).

The central part of the apparatus was the reaction cell which consisted of a stainless-steel cylinder with an inner ceramic cylinder through which the photolysis and the probe laser beam counter-propagated. In order to minimise scattered light, the laser beams were passed through a system of special light baffles. The ceramic cylinder was heated with a resistive tantalum wire. The temperature in the reaction cell was measured by two shielded, calibrated and movable thermocouples. Details of the reaction cell are given elsewhere.^{7,13}

The pressure in the reaction cell was measured with capacitance manometers directly at the cell exit. In the experiments the flow velocity of the gas mixture was $<0.5 \text{ m s}^{-1}$ to avoid accumulation of photolysis products in the observation zone. The NCO fluorescence was detected at right-angles to the laser beams by a photomultiplier (EMI 1P28) through a lens system and an interference filter with a maximum transmission at 440 nm. The photomultiplier output was integrated by an SRS box car averager (Model SR 250), digitised and then analysed by an ATARI Mega ST microcomputer.

All gases employed were supplied either by Messer Griessheim or by Merck-Schuchardt and were used without further purification. The purities of the gases used were 99.998% (Ar), 97.0% (allene), 99.0% (but-1-ene), 95.0% (but-1-yne), 99.95% (ethane) and 99.5% (propene). CINCO, which was stored in 20 l glass bulbs diluted in argon in the ratio 1 : 250, was prepared by thermal decomposition of $(\text{CINCO})_3$ (Merck, >98%) and was purified by trap-to-trap distillation.¹⁴ The concentrations of the gases were determined by their partial flows measured by calibrated flow meters (Tylan FM 360) with an accuracy of $\sim 2\%$.

3. Results and discussion

The reactions were investigated under pseudo-first-order conditions, *i.e.*, the NCO concentration was much lower than that of the hydrocarbons. This was achieved by keeping the concentration of the reactants always at least 20 times larger than that of CINCO, the precursor of NCO. Accordingly, the NCO concentration time profiles can be described as follows:

$$[\text{NCO}]_t = [\text{NCO}]_{t=0} \exp[-kt]$$

$$k = k_i[\text{X}_i] + k_0$$

where $[\text{X}_i]$ is the concentration of the hydrocarbon i , k_i is the corresponding bimolecular rate coefficient of the reaction $\text{NCO} + \text{X}_i$ and the decay rate k_0 is the first-order decay constant in the absence of any added reactant. Under these conditions, the NCO decay is mainly caused by reactions with CINCO, photolysis products and by diffusion out of the observation zone.

Fig. 1 is a typical plot of the natural logarithm of the relative $[\text{NCO}]$ as a function of the reaction time for different reactant concentrations of C_2H_6 . Pseudo-first-order decay constants k were derived from the slope of the individual straight line plots. The values of k increased proportionally with the concentration of reactant added. By subtracting the decay constants k_0 , which were determined from the measurements without any reactant added, from the corresponding k values obtained in the presence of the reactant, corrected pseudo-first-order decay constants $k'_{\text{corr.}}$ were obtained. The bimolecular rate coefficient $k_{\text{NCO}+\text{X}_i}$ for a given temperature and pressure was then obtained by plotting $k'_{\text{corr.}}$ as a function of the reactant concentration, as shown in Fig. 2 taking C_2H_6 as an example. For all experiments carried out, the reactant concentrations were varied by a factor of at least 9.

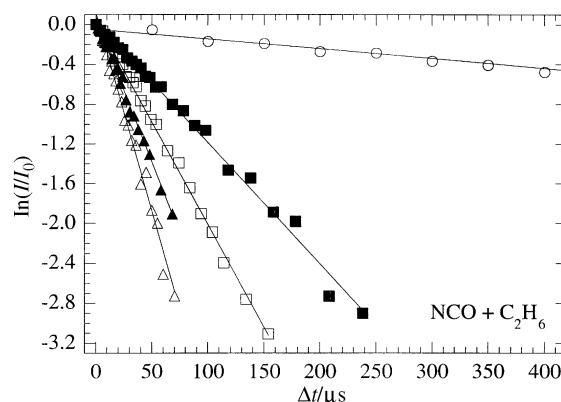


Fig. 1 Semi-logarithmic plot of the NCO decay after excimer laser photolysis of $9.1 \times 10^{12} \text{ cm}^{-3}$ CINCO at $T = 755 \text{ K}$ and 20 Torr total pressure in argon in the presence of different C_2H_6 concentrations (10^{17} cm^{-3}): (○) 0; (■) 1.2; (□) 2.2; (▲) 3.3 and (△) 4.4.

3.1 The reaction of NCO radicals with ethane

The $\text{NCO} + \text{C}_2\text{H}_6$ reaction was investigated in the temperature range 297–899 K at 20 Torr total pressure and at 651 K in the pressure range 5–528 Torr. The bimolecular rate coefficients obtained are presented in Fig. 3 as an Arrhenius plot and are summarised in Tables 1 and 2 together with literature data. The given rate coefficients are weighted means of

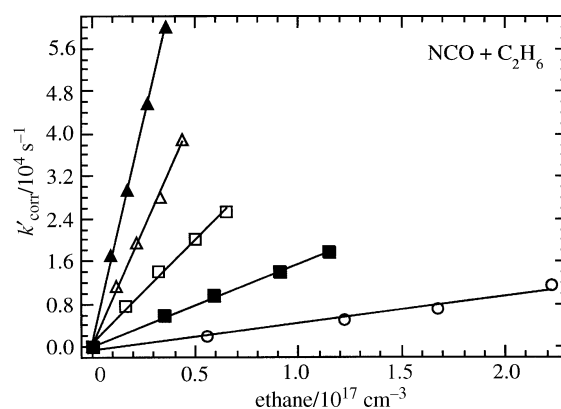


Fig. 2 Plot of pseudo-first-order decay constants k'_{corr} of NCO radicals vs. the concentrations of ethane at 20 Torr total pressure in argon for different temperatures: (○) 371; (■) 462; (□) 651; (△) 755; and (▲) 899 K.

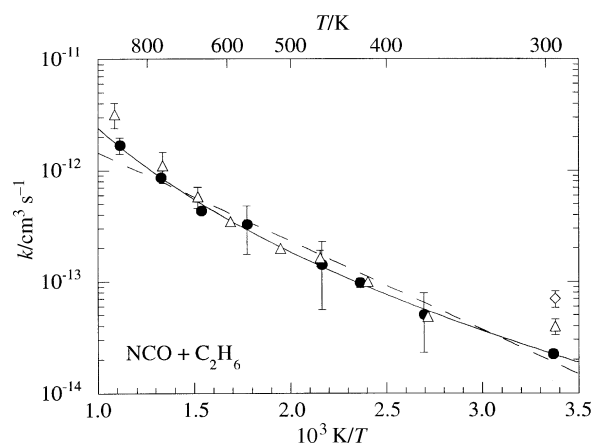


Fig. 3 Temperature dependence of the bimolecular rate coefficient $k_{\text{NCO}+\text{C}_2\text{H}_6}$ for the $\text{NCO} + \text{C}_2\text{H}_6$ reaction: (◇) Park and Hershberger;¹⁵ (◆) Schuck *et al.*;¹² (●) this work. The lines are different least squares fits to the data obtained in this work (see Table 2): solid line, modified three parameter Arrhenius equation; and dashed line, simple Arrhenius equation.

Table 1 Bimolecular rate coefficients $k_{\text{NCO}+\text{C}_2\text{H}_6}$ for the reaction $\text{NCO} + \text{C}_2\text{H}_6 \rightarrow \text{products}$ as a function of the total pressure at 651 K. The error limits represent the 90% confidence interval and reflect the statistical precision only

Pressure/ Torr	No. of experiments	$k_{\text{NCO}+\text{C}_2\text{H}_6}/$ $10^{-13} \text{ cm}^3 \text{ s}^{-1}$
5.1	3	5.26 ± 1.84
10.3	7	5.15 ± 0.42
20.6	3	3.85 ± 0.24
100.5	3	4.96 ± 0.57
295.5	5	3.63 ± 1.24
527.5	4	3.71 ± 0.61

at least five k -values which were determined in independent measurements using at least five different reactant concentrations. Fig. 3 shows a positive temperature dependence with a slightly upward curvature. Using the simple Arrhenius expression, $k(T) = A \exp(-E_A/RT)$, the rate coefficients is described by

$$k_{\text{NCO}+\text{C}_2\text{H}_6}(T) = (9.0 \pm 1.0) \times 10^{-12} \times \exp[-(15.2 \pm 0.4)/RT] \text{ cm}^3 \text{ s}^{-1}$$

with E_A in kJ mol^{-1} . However, a much better description is provided by the following modified three-parameter Arrhenius expression of the form $k(T) = B(T/298)^n \exp(-E_0/RT)$ obtained by weighted non-linear least squares procedures using the inverse squares of experimental errors of the rate

Table 2 Bimolecular rate coefficients $k_{\text{NCO}+\text{C}_2\text{H}_6}$ for the reaction $\text{NCO} + \text{C}_2\text{H}_6 \rightarrow \text{products}$ as a function of temperature at 20 Torr total pressure. The error limits represent the 90% confidence interval and reflect the statistical precision only

Temperature/ K	No. of experiments	$k_{\text{NCO}+\text{C}_2\text{H}_6}/$ $10^{-13} \text{ cm}^3 \text{ s}^{-1}$	Ref. ^a
296		0.40 ± 0.06	12
296		0.70 ± 0.12	15
297	5	0.21 ± 0.02	This work
368		0.48 ± 0.05	12
371	3	0.51 ± 0.28	This work
416		0.99 ± 0.09	12
423	5	0.98 ± 0.09	This work
462	3	1.42 ± 0.86	This work
464		1.63 ± 0.26	12
513		1.98 ± 0.12	12
564	3	3.27 ± 1.51	This work
592		3.47 ± 0.20	12
651	25	4.34 ± 0.30^b	This work
659		5.83 ± 1.26	12
749		11.13 ± 3.45	12
755	4	8.65 ± 0.52	This work
899	3	16.90 ± 2.80	This work
922		32.05 ± 8.14	12

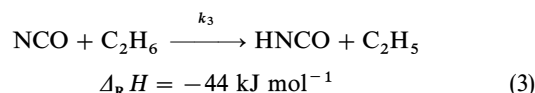
^a Data from Park and Hershberger¹⁵ measured at 6.6 Torr total pressure; data from Schuck *et al.*¹² measured in the pressure range 44–72 Torr. ^b Measured in the pressure range 5–528 Torr.

coefficients as statistical weight (the errors were estimated by variation of the coefficients):

$$k_{\text{NCO}+\text{C}_2\text{H}_6}(T) = (6.2^{+3.8}_{-3.7}) \times 10^{-14} (T/298)^{(3.27 \pm 0.84)} \times \exp[-(2.5^{+3.4}_{-2.3})/RT] \text{ cm}^3 \text{ s}^{-1}$$

with the minimum collision energy at which the reaction occurs, E_0 in kJ mol^{-1} . The $\text{NCO} + \text{C}_2\text{H}_6$ reaction showed no pressure dependence in the range 5–528 Torr at 651 K. Both the positive temperature dependence and the pressure independence indicate that the $\text{NCO} + \text{C}_2\text{H}_6$ reaction proceeds as a simple H atom abstraction reaction.

These results are in good agreement with literature data.^{12,15} Park and Hershberger¹⁵ determined a bimolecular rate coefficient of $(7.01 \pm 1.20) \times 10^{-14} \text{ cm}^3 \text{ s}^{-1}$ at room temperature using infrared diode laser spectroscopy. They observed HNCO as a reaction product which is consistent with the proposed simple H atom abstraction:



A more detailed kinetic investigation of the $\text{NCO} + \text{C}_2\text{H}_6$ reaction was carried out by Schuck *et al.*¹² in the range 296–922 K at total pressures in the range 44–72 Torr. In agreement with the findings in the present study, they observed a positive temperature dependence with a slight curvature in the Arrhenius plot which is well described by the following three-parameter Arrhenius expression:

$$k_{\text{NCO}+\text{C}_2\text{H}_6}(T) = 2.69 \times 10^{-16} (T/298)^{(6.89 \pm 0.02)} \times \exp[(12.2 \pm 0.5)/RT] \text{ cm}^3 \text{ s}^{-1}$$

However, it should be pointed out that Schuck *et al.*¹² reported a room temperature rate coefficient which is twice the value measured in the present study. In addition, the k values of Schuck *et al.*¹² exhibit a more pronounced curvature in the Arrhenius plot. This stronger curvature is mainly caused by the rate coefficient measured by Schuck *et al.* at room temperature, which is significantly higher than the value obtained in the present work. Schuck *et al.*¹² reported a threshold energy E_0 of $-(12.2 \pm 0.5) \text{ kJ mol}^{-1}$ by fitting the three-parameter Arrhenius expression to their data. A negative threshold energy makes no sense physically. Moreover, there is no evidence that the energy parameter in a three-parameter expression for $k(T)$ corresponds to the threshold energy of a reaction. Accordingly, it might be concluded that the modified Arrhenius expression obtained from the present study provides a better description of the temperature dependence of the $\text{NCO} + \text{C}_2\text{H}_6$ reaction than that of Schuck *et al.*¹²

Since the NCO radical is a pseudo-halogen, it is reasonable to compare the rate coefficients from the present study with literature data for the corresponding reactions with halogen atoms and other pseudo-halogens. Table 3 summarises the Arrhenius parameters known for these reactions. All reactions proceed as simple H atom abstractions. The rate coefficients

Table 3 Arrhenius parameters for the reactions of $\text{C}_2\text{H}_6 + \text{X}$ ($\text{X} = \text{NCO}, \text{OH}, \text{CN}, \text{F}, \text{Cl}, \text{Br}$ and I)

Reactant R	Pressure/ Torr	Temperature/ K	$A/$ $\text{cm}^3 \text{ s}^{-1}$	E_0 or $E_A/$ kJ mol^{-1}	Ref.
NCO	20	297–899	$6.2 \times 10^{-16} \times (T/298)^{3.27}$	2.5	This work
OH	—	250–2000	$1.06 \times 10^{-12} \times (T/298)^2$	3.6	4
CN	50–500	185–739	$1.36 \times 10^{-11} \times (T/298)^{1.26}$	–1.7	16
F	200	210–363	7.1×10^{-11}	2.9	17
Cl	10	292–600	8.59×10^{-11}	1.1	18
Br	100	473–621	2.35×10^{-11}	53.3	19
I	4	503–618	2.21×10^{-10}	110.5	20

increase with increasing reaction enthalpy. As observed in previous studies^{8,9} the kinetic behaviour of NCO radicals is similar to that of OH radicals. The rate coefficients of both reactions exhibit a positive temperature dependence with a curvature in the Arrhenius plot. The reactions have similar activation energies and comparable rate coefficients at room temperature.

3.2 Reactions of NCO radicals with unsaturated hydrocarbons

The reactions of NCO with C₃H₄, C₃H₆, C₄H₈ and C₄H₆ were studied at room temperature and 20 Torr total pressure. In addition, the NCO + C₃H₄ reaction was investigated in the pressure range 21–39 Torr, and the NCO + C₄H₆ reaction in the pressure range 21–102 Torr. The results are summarised in Table 4 together with literature values.

The NCO + C₃H₄ and NCO + C₄H₆ reactions exhibit no pressure dependence within the investigated ranges. Considering the data of Wategaonkar and Setser¹¹ for the NCO + C₃H₆ reaction, the rate coefficient $k_{\text{NCO}+\text{C}_3\text{H}_6}$ exhibits a pressure dependence in the range 0.6–21 Torr.

However, the pressure independence of the NCO + C₃H₄ and NCO + C₄H₆ reactions in the pressure range investigated is not inconsistent with the prediction that the reactions of NCO radicals with unsaturated hydrocarbons are addition reactions for which a pressure dependence is expected. It is possible that these reactions have reached their high-pressure

limit at pressures of about 20 Torr because the adducts formed have more degrees of freedom among which the reaction energy can be distributed. It has been observed, for example, that the adduct which is formed in the NCO + C₂H₄ reaction reached its high-pressure limit at pressures of about 100 Torr.

The rate coefficients of the NCO reactions with unsaturated hydrocarbons are of the order of magnitude of 10^{-11} cm³ s⁻¹ and, therefore, are as fast as NCO radical reactions with NO, H and O atoms.^{4,7} These species are considered to be the most important reaction partners of NCO radicals in combustion processes. However, the present results suggest that the reactions of NCO radicals with unsaturated hydrocarbons can possibly compete with reactions of NCO with NO and atoms in combustion processes, particularly under fuel-rich conditions.

The rate coefficient obtained can be compared with rate parameters of the corresponding reactions of the investigated hydrocarbons with other pseudo-halogens and halogen atoms, the data for which are summarised in Table 5 together with the results of the present study. Again, a similar behaviour of NCO and OH radicals was observed. The rate coefficients for both radicals reacting with the hydrocarbons investigated are of the same order of magnitude. In addition, the OH + hydrocarbon reactions proceed as addition reactions, which has been also suggested for the corresponding NCO reactions.

Table 4 Bimolecular rate coefficients for reactions of NCO radicals with selected reaction partners and the ionisation potentials of the reactants R taken from ref. 11

Reactant R	Pressure/ Torr	IP/ eV	$k_{\text{NCO}+\text{R}}/cm^3 s^{-1}$	Ref.
Ethene	0.6	10.507	$(1.23 \pm 0.12) \times 10^{-12}$	11
Ethene	6.6	10.507	$(2.85 \pm 0.22) \times 10^{-12}$	15
Ethene	25	10.507	$(3.78 \pm 0.38) \times 10^{-12}$	21
Ethene	20	10.507	3.76×10^{-12}	8
Ethyne	0.6	11.4	$(1.9 \pm 0.2) \times 10^{-13}$	11
Ethyne	6.6	11.4	$(7.47 \pm 0.80) \times 10^{-14}$	15
Ethyne	20	11.4	$(1.11 \pm 0.04) \times 10^{-13}$	9
Allene	21–39	9.690	$(1.39 \pm 0.18) \times 10^{-11}$	This work
Propene	21	9.730	$(4.29 \pm 0.20) \times 10^{-11}$	This work
Propene	0.6	9.730	1.05×10^{-11}	11
But-1-ene	22	9.580	$(6.18 \pm 0.46) \times 10^{-11}$	This work
But-1-yne	21–102	10.178	$(1.41 \pm 0.14) \times 10^{-11}$	This work
(E)-Butadiene	0.6	9.069	$(2.35 \pm 0.11) \times 10^{-11}$	11
NO	0.6	9.2644	$(3.32 \pm 0.08) \times 10^{-11}$	11
NO	10	9.2644	$(5.0 \pm 0.2) \times 10^{-11}$	7
NO ₂	0.6	9.75	$(7.52 \pm 0.49) \times 10^{-12}$	11

Table 5 Bimolecular rate coefficients of the reactions of C₃H₄, C₃H₆, C₄H₆ and C₄H₈ + X (X = NCO, OH, CN, F, Cl, Br and I) at room temperature

Reaction	Pressure/ Torr	Temperature/ K	$k/cm^3 s^{-1}$	Ref.
C ₃ H ₄ + NCO	21–39	293	$(1.39 \pm 0.18) \times 10^{-11}$	This work
C ₃ H ₄ + OH	760	293	9.43×10^{-12}	22
C ₃ H ₄ + CN	760	293	4.65×10^{-10}	23
C ₃ H ₄ + Cl	760	295	$(4.38 \pm 0.26) \times 10^{-10}$	24
C ₃ H ₆ + NCO	21	293	$(4.29 \pm 0.20) \times 10^{-11}$	This work
C ₃ H ₆ + OH	760	298	3.01×10^{-11}	25
C ₃ H ₆ + CN	760	293	1.22×10^{-10}	26
C ₃ H ₆ + F	1–70	298	4.48×10^{-11}	27
C ₃ H ₆ + Cl	760	295	$(3.22 \pm 0.13) \times 10^{-10}$	24
C ₃ H ₆ + Br	760	298	$(2.7 \pm 0.5) \times 10^{-12}$	28
C ₃ H ₆ + I	47–506	293	1.0×10^{-24}	29
C ₄ H ₈ + NCO	22	294	$(6.18 \pm 0.46) \times 10^{-11}$	This work
C ₄ H ₈ + OH	735	295	$(3.13 \pm 0.16) \times 10^{-11}$	30
C ₄ H ₈ + Br	760	298	$(3.4 \pm 0.7) \times 10^{-12}$	28
C ₄ H ₈ + I	28–68	294	1.7×10^{-21}	31
C ₄ H ₆ + NCO	21–102	293	$(1.41 \pm 0.14) \times 10^{-11}$	This work
C ₄ H ₆ + OH	1.7–6.4	293	7.1×10^{-12}	32
C ₄ H ₆ + Cl	760	295	$(3.39 \pm 0.12) \times 10^{-10}$	24

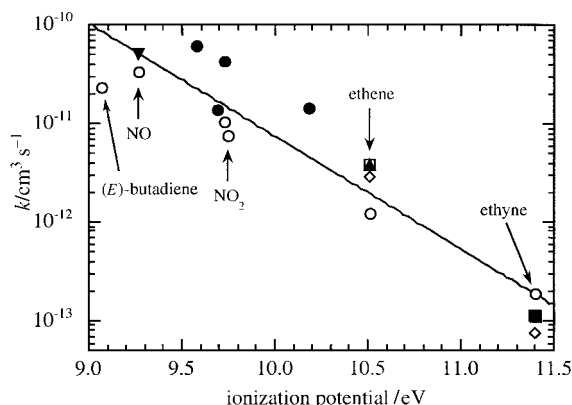


Fig. 4 Correlation between the bimolecular rate coefficients of the NCO reactions with unsaturated hydrocarbons, NO and NO₂ and the ionisation potentials of these compounds: (□) Perry;²¹ (■) Becker *et al.*;⁹ (○) Wategaonkar and Setser;¹¹ (▲) Becker *et al.*;⁸ (▼) Becker *et al.*;⁷ and (●) this work. The solid line is a least squares linear fit to all data listed in Table 4.

3.3 Correlation of bimolecular rate coefficients of the reactions of NCO radicals with unsaturated compounds and their ionisation potentials

The bimolecular rate coefficients obtained in the present study are presented in Fig. 4 together with literature values^{7,8,9,11,21} for unsaturated hydrocarbons and for NO and NO₂ as a function of the ionisation potential of the different reaction partners. This correlation was proposed by Wategaonkar and Setser.¹¹ All data are summarised in Table 4. The plot shows a good correlation between the order of magnitude of the rate coefficients and the ionisation potentials (IP). A linear fit to all data leads to the following expression:

$$\ln k_{\text{NCO}+\text{R}} = -(2.64 \pm 0.25)IP_{\text{R}} + (0.73 \pm 2.27)$$

The obtained increase in the rate coefficients with decreasing ionisation potential of the unsaturated compounds is expected for addition reactions. This observation can be explained by the easier polarisation made possible through the electrophilic attack of the NCO radical on the multiple bond of the reaction partner.

4. Summary and conclusions

The reaction of NCO radicals with C₂H₆ was studied over wide temperature and pressure ranges. The reaction was found to be independent of pressure. The bimolecular rate coefficients exhibit a positive temperature dependence with a slight curvature in the Arrhenius plot. The results lead to the conclusion that the NCO + C₂H₆ reaction proceeds as a simple H abstraction forming HNCO and C₂H₅ as products, which is in good agreement with literature data.

The rate coefficients for the reactions of NCO radicals with C₃H₄, C₃H₆, C₄H₆ and C₄H₈ were determined at room temperature. All values of *k* are of the order of magnitude of 10⁻¹¹ cm³ s⁻¹ and are as fast as the reactions of NCO with NO, H and O atoms, which are suggested to be the major sinks for NCO radicals in combustion processes. Therefore, the reactions of NCO radicals with these hydrocarbons may compete in combustion processes, especially under fuel-rich conditions, with the important NCO reactions mentioned above and should be involved in combustion modelling.

A correlation between the bimolecular rate coefficients of NCO reactions with unsaturated compounds and the ionisation potential of these species was established. The increase in the rate coefficients with decreasing ionisation potential suggests that these reactions proceed as addition reactions.

Further studies of the temperature and pressure dependence of the NCO reactions with unsaturated hydrocarbons would

be useful to establish further the importance of these reactions in combustion processes. In addition, the confirmation of the correlation between the rate coefficients of NCO reactions with unsaturated hydrocarbons and the ionisation potential of these reactants at higher temperatures would provide a method to predict unknown rate parameters of NCO reactions with unsaturated compounds at combustion temperatures.

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