NCO: a potential interstellar species

Sheo S. Prasad and Wesley T. Huntress, Jr

Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, California 91103, USA

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Summary. The molecule NCO may exist in dense interstellar clouds with a fractional abundance between $3 \times 10^{-10}$ and $6 \times 10^{-9}$. Its observation would provide an estimate of the abundance of $O_2$. It may also contribute to the formation of isocyanic acid.

The objective of this communication is to draw attention to the possible significant concentration of NCO radicals in dark, dense interstellar clouds. The NCO radicals may be synthesized in these clouds by the reaction:

$$CN + O_2 \rightarrow NCO + O.$$  \hspace{1cm} (1)

Measurements of the rate coefficient, $k_1$, of reaction (1) at 300 and 687 K (Basco 1965; Boden & Thrush 1968) showed that it may have only a small activation energy and value of $7 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ is possible at the low temperatures characteristic of interstellar clouds. Molecular oxygen has not been detected in interstellar clouds but theoretical studies predict appreciable concentrations. Using a very simple model, Herbst & Klemperer (1973) obtained $f_{O_2} = 4 \times 10^{-7}$ for $n(H_2) = 3 \times 10^5$ cm$^{-3}$. Subsequent theoretical models (e.g. Mitchell, Ginsburg & Kuntz 1977; Prasad & Huntress, in preparation) predict a much higher $f_{O_2} \sim 1 - 7 \times 10^{-5}$ for dark clouds with $10^4 < n < 10^6$ cm$^{-3}$ using more realistic elemental depletion (Morton 1975) and a comprehensive chemical reaction network. The fractional abundance of CN in dense clouds is on the order $f_{CN} \sim$ a few $\times 10^{-9}$ (Turner & Gammon 1975; Turner & Thaddeus 1977). Using the values $f_{CN} = 2 \times 10^{-9}$ and $f_{O_2} = 10^{-5}$, the production rate for NCO, $q(NCO) = 5.6 \times 10^{-15}$ cm$^{-3}$ s$^{-1}$ for dense clouds with $(nH_2) = 2 \times 10^5$ cm$^{-3}$. To obtain the equilibrium number density of NCO from $q(NCO)$, the loss rate must be calculated.

The loss mechanisms for NCO appear to be:

$$\text{He}^+ + \text{NCO} \rightarrow \text{CO}^+ + \text{N} + \text{He}$$  \hspace{1cm} (2a)

$$\rightarrow \text{other products} + \text{He}$$  \hspace{1cm} (2b)

$$(\text{H}_3^+, \text{HCO}^+, \text{H}_3\text{O}^+) + \text{NCO} \rightarrow \text{HNCO}^+ + (\text{H}_2, \text{CO}, \text{H}_2\text{O})$$  \hspace{1cm} (3)

From the experimental work of Dixon (1960), the photodestruction of NCO is likely to be fast in diffuse clouds. NCO is, therefore, not likely to be present in large fraction abundance in optically-thin clouds. In dark clouds, however, reaction (8) can be ignored. The ionic reactions (2) to (4) most likely proceed rapidly with rate coefficients of about $10^{-9}$ cm$^{-3}$ molecule$^{-1}$ s$^{-1}$. Theoretical calculations (Mitchell et al. 1977; Prasad & Huntress, in preparation) indicate that the atomic ions C$^+$ and He$^+$ are at least a factor of 2 to 3 smaller in abundance compared to the polyatomic H$_2^+$ and HCO$^+$. HCO$^+$ ions have been observed in dense clouds and the observations reported by Turner & Thaddeus (1977) suggest that HCO$^+$/HC$_3$N is less than, or at best about equal to, unity in clouds with $10^4 < n < 3 \times 10^5$ cm$^{-3}$. On this basis $f_{\text{HCO}} \approx 8 \times 10^{-10}$ for $10^5 < n(\text{H}_2) < 10^6$ and $34 \text{K} < T < 65 \text{K}$ (Clark, Buhl, & Snyder 1974) leads to a combined fractional abundance of about $2 \times 10^{-9}$ for all the ions involved in reactions (2) to (4). This result yields a loss rate-coefficient for ionic processes per NCO radical L$^+$ (NCO), of about $4 \times 10^{-13}$ s$^{-1}$ molecule$^{-1}$. For dense clouds, however, L$^+$ (NCO) is about an order of magnitude smaller than the loss due to condensation on to grains, reaction (9), $L^8 (\text{NCO}) \approx 4.7 \times 10^{-12}$ s$^{-1}$ calculated using the expression given by Herbst & Klempner (1973).

To calculate the loss due to neutral reactions, we require the rate constants for the atomic reactions (6) and (7). Reaction (5) can be ignored due to the low concentration of free atomic carbon relative to N and O. There are no experimental data for the rate constant $k_6$ or $k_7$. Both reactions (6) and (7) are radical-atom reactions so that if the customary assumption (Herbst & Klempner 1973) is made that these reactions have no activation energy barrier then, at interstellar temperatures, we may assign $K_6 = K_7 = 10^{-11}$ cm$^{-3}$ molecule$^{-1}$ s$^{-1}$. Under these circumstances the neutral reactions (6) and (7) dominate both the ion and grain loss and yield a loss rate-coefficient $L^9 (\text{NCO}) \approx 10^{-10}$ s$^{-1}$ based upon an illustrative value $(n(\text{O}) + n(\text{N})) = 10$ cm$^{-3}$. This latter value is probably a reasonable choice for our present purpose in view of the values 6.7 and 12 cm$^{-3}$ predicted for $n(\text{O}) + n(\text{N})$ by Mitchell et al. (1977) and Prasad & Huntress for $n(\text{H}_2) = 2 \times 10^5$ cm$^{-3}$ and $T = 60$ K. This estimated $L(\text{NCO})$ will result in an NCO concentration $n(\text{NCO}) \approx 5.6 \times 10^{-5}$ cm$^{-3}$ and $f_{\text{NCO}} \approx 2.8 \times 10^{-10}$ in a model dense cloud with $n(\text{H}_2) = 2 \times 10^5$ cm$^{-3}$.

It may be unreasonable to assume zero activation for the reactions (6) and (7). There are very few measurements, but a recent critical survey of reaction-rate data (Hudson 1977) shows that an activation energy of $\sim 0.5$ kcal/mole is a number which is appropriate to man reactions of reactive atoms with radical triatomic species. For an activation energy of 0. kcal/mole or greater, the loss rate of NCO by neutral reactions becomes less than loss b condensation on to the grains for $T < 60$ K. Under these circumstances $n(\text{NCO}) \approx 1.2 \times 10^{-7}$ cm$^{-3}$ and $f_{\text{NCO}} \approx 6 \times 10^{-9}$. The fractional abundance of NCO is therefore predicted to be in the range $3 \times 10^{-10} < f_{\text{NCO}} < 6 \times 10^{-9}$ for dense clouds with $n(\text{H}_2) \approx 2 \times 10^5$ cm$^{-3}$ and $T < 60$ K such as the Orion molecular cloud. For lower sticking probability of NCO on to grains, the upper limit becomes even larger. On the other hand, the time required for reachin...
the estimated equilibrium concentrations could be large compared to other time constants of interest, i.e. that of gravitational collapse. In this case both upper and lower bounds may be overestimates. Nevertheless, the range of predicted $f_{\text{NCO}}$ would still justify an attempt to search for NCO.

A search for NCO in dense clouds is important for several reasons. In addition to NCO itself, a detection of NCO would constitute an indirect measurement of molecular oxygen. A determination of the $O_2$ abundance in dark clouds has special significance in view of the previously mentioned large difference in $f_{O_2}$ predicted by earlier simple models and more recent comprehensive calculations. Herbst et al. (1977) examined the possibility of $O_2$ abundance measurement via the observation of $f_{\text{HO}}$, but concluded that this may not succeed. We therefore propose an alternative prospect for $O_2$ measurement. All important parameters involved (i.e. $k_1$, $k_6$, $k_7$) can be accurately determined in the laboratory to confirm the chemical scheme proposed.

NCO might possibly be a precursor in the synthesis of isocyanic acid, HNCO, which has been observed in interstellar clouds with $f_{\text{HNCO}} \sim 10^{-10}$ (Watson 1976). This synthesis of HNCO from NCO may involve reaction (3), followed by

$$\text{HNCO}^+ + \text{H}_2 \rightarrow \text{H}_2 \text{NCO}^+ + \text{H} \quad (10)$$

and

$$\text{H}_2 \text{NCO}^+ + \text{e}^- \rightarrow \text{HNCO} + \text{H}. \quad (11)$$

Should laboratory studies prove reaction (10) to be slow, HNCO formation would still be possible by radiative recombination of HNCO with electrons or by charge transfer from HNCO$^+$ to metals.

Efficient destruction of HNCO by neutral reactions is probably unlikely in the cold interstellar environment. It is more likely to be destroyed by ion–molecule reactions or by condensation on to grains. Considering the previously mentioned estimated densities for ions such as He$^+$ and H$_3^+$, which might react with HNCO, it appears that grain depletion may dominate even for a sticking probability of 10 per cent. This assumption yields a loss rate constant $L(\text{HNCO}) \sim 5 \times 10^{-13}$ s$^{-1}$ molecule$^{-1}$ in dense clouds with $n(\text{H}_2) = 2 \times 10^5$ cm$^{-3}$.

If both reactions (3) and (10) are rapid with rate coefficients of $\sim 10^{-9}$ cm$^{-3}$ molecule$^{-1}$ s$^{-1}$, then $n(\text{HNCO}) \sim 0.1 \, n(\text{NCO})$ in equilibrium. On the other hand, if only reaction (3) is rapid, then $n(\text{HNCO}) \sim 10^{-4} \, n(\text{NCO})$. It is worth noticing that the latter ratio can be maintained even if none of the ion–molecule reactions (2), (3), (10) or (11) occur and if HNCO is synthesized by radiative association of NCO with the residual hydrogen atoms:

$$\text{H} + \text{NCO} \rightarrow \text{HNCO} + \text{h} \nu \quad (12)$$

with a rate coefficient of about $2.5 \times 10^{-17}$ cm$^{-3}$ molecule$^{-1}$ s$^{-1}$. These estimates, combined with a possible $f_{\text{NCO}} \sim 10^{-9}$, lead to the relations $10^{-13} < f_{\text{HNCO}} < 10^{-10}$ for clouds with $n(\text{H}_2) = 2 \times 10^5$ cm$^{-3}$. A larger concentration for HNCO would result from a sticking probability of less than 10 per cent. Thus the observed $f_{\text{HNCO}} \sim 10^{-10}$ falls within our predictions. This result may be of some significance in assessing the contributory role of other mechanisms for HNCO synthesis in interstellar clouds.

On the basis of the above discussions we suggest that a search for NCO in dark, dense clouds is warranted. The Orion molecular cloud is suggested as a possibility. Sgr B$_2$ may not be a good source of NCO because it appears to be underabundant in CN (Turner & Gammon 1975). The microwave spectrum of NCO reported by Sato & Amano (1970) contains two lines at 58160 and 81413 MHz due to the $J = 3/2 \rightarrow 5/2$ and $J = 5/2 \rightarrow 7/2$ transitions, respectively, of the $^2\Pi_{3/2}$ ground state. The line at 80413 MHz was relatively stronger and may be more suitable for the suggested search (Kakar, private communications). Accurate laboratory
determinations should be made of the rate constants for the reactions important in NC
and HNCO production and loss.

(A couple of weeks after the original manuscript was dispatched to the editor, a study of
molecule formation in interstellar clouds by Iglesias (1977) came to our attention. In that
study Iglesias also proposes formation of interstellar NCO via the reaction CN + O2
NCO + O. However, there are several differences between our work and Iglesias’ study. The
treatment of the NCO loss mechanism in Iglesias’ study appears less comprehensive than
ours. The initiation of HNCO formation through the He+ + NCO → NCO+ + He, suggested by
Iglesias, may be questionable. Above all, neither the feasibility nor the astrophysical signif-
cance of a detection of NCO was discussed by Iglesias.)

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