Tetrahedron Letters No.39, pp. 4177-4180, 1968. Pergamon Press. Printed in Great Britain.

# REACTION OF CARBENES WITH MOLECULAR NITROGEN

A.E.Shilov, A.A.Shteinman, M.B.Tjabin

Institute of Chemical Physics of Academy of Sciences of USSR, Moscow

(Received in UK 15 April 1968; accepted for publication 3 July 1968)

It has been discovered recently that molecular nitrogen undergoes comparatively fast reactions with $CH_2$ in a solid matrix at 20°K (1) and in the gas phase at 300°K (2) with CH (3), C (4) and O(5). These active particles can exist in singlet and triplet states, the latter being the ground state.

We have shown previously (2) that noticeable amounts of $CH_2N_2^{15}$ were formed in partial thermal and photochemical decomposition of $CH_2N_2$ in the atmosphere of $N_2^{15}$ by the mechanism:

$$CH_2N_2^{14} \xrightarrow{\Delta \text{ or } h\nu} CH_2 + N_2^{14} \qquad CH_2 + N_2^{15} \longrightarrow CH_2N_2^{15}$$

Mass- and i.r.spectrometry were used to detect $CH_2N_2^{15}$. I.r.spectrum of diazomethane, separated from the products of partial photolysis of $CH_2N_2^{14}$ in $N_2^{15}$ at 700 mm Hg shows, together with a remaining band at 2096 $cm^{-1}$ corresponding to $CH_2N_2^{14}$, a distinct band at 2020 $cm^{-1}$ due to $CH_2N_2^{15}$ (FIG.1). Mass-spectrum of nitrogen obtained from this product indicates considerable amounts of $N_2^{15}$. There is a good qualitative agreement between results obtained by the two methods (FIG.1).

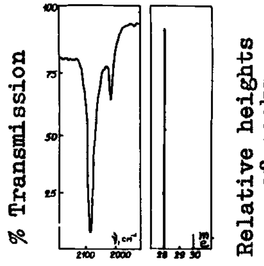


FIG. 1

It should be mentioned that Wilson and Kistiakowsky(6) and more recently Moore and Pimentel (1) came to the conclusion that $CH_2$ does not react with $N_2$ in the gas phase. Presumably this is due to unsufficient sensitivity of analysis used by these workers.

The ratio of $CH_2N_2^{15}$ formed to the diazomethane decomposed (f) rises with decrease in initial concentration of $CH_2N_2^{14}$, decrease in temperature and increase in pressure of $N_2^{15}$.

The photolysis and the pyrolysis of $CH_2N_2^{14}$ in $N_2^{15}$ can be expressed by the following sequence of reactions:

$$CH_2N_2 + (M) \longrightarrow CH_2(s) + N_2 + (M) \qquad CH_2(s) + M \longrightarrow CH_2(t) + M$$

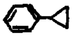
$$CH_2(s) + N_2^{15} + M \longrightarrow CH_2N_2^{15} + M \qquad CH_2(t) + N_2^{15} + M \longrightarrow CH_2N_2^{15} + M$$

$$CH_2(s) + CH_2N_2 \longrightarrow C_2H_4 + N_2 \qquad CH_2(t) + CH_2(t) + M \longrightarrow C_2H_4 + M$$

M is a molecule of an inert activator or deactivator, $M = N_2, CH_2N_2, C_2H_4$.

We have found (2c) that $CH_2(t)$ is less reactive towards $N_2$ than $CH_2(s)$. The activation energies of reactions of $CH_2(t)$ and $CH_2(s)$ with molecular nitrogen are about 16 and 8 kcal/mole, respectively.

TABLE 1

| Source of $CH_2$ | $f \cdot 10^3$ |
|---|---|
| $CH_2N_2$ | 85 |
| $CH_2{<}\begin{smallmatrix}N\\ N\end{smallmatrix}$ | 40 |
| $CH_2CO$ | >4 |
|  | >7 |

The photolyses of diazirine, ketene and phenylcyclopropane in $N_2^{15}$ have been studied then; the above substances also are known to be possible sources of $CH_2$ (7a,b). In all cases the formation of $CH_2N_2^{15}$ was detected with the isotopic dilution method (TABLE 1).

Because of frequent explosions when handling with diazirine, only few experiments have been performed with the irradiation time of 60 and 90 min, $P^o_{CH_2{<}\begin{smallmatrix}N\\ N\end{smallmatrix}} = 1 - 2$ mm Hg and $P_{N_2^{15}} = 660$ mm Hg (TABLE 2).

TABLE 2

| $n^o_{CH_2{<}\begin{smallmatrix}N\\ N\end{smallmatrix}}$ (mmHg)* | $\alpha$ | $n_{CH_2N_2}$ (mmHg)** | $N_2^{15}/\Sigma N_2 \cdot 100$ from $CH_2N_2$ | $N_2^{15}/\Sigma N_2 \cdot 100$ from $CH_2{<}\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix}$ | $f(CH_2{<}\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix})$ | |
|---|---|---|---|---|---|---|
| 18.0 | 0.480 | 14.0 | 0.848 | 0.009 | 0.0201 | $f = \dfrac{N_2^{15}/\Sigma N_2 \cdot n_{CH_2N_2}}{\alpha \cdot n^o_{CH_2{<}\begin{smallmatrix}N\\ \|\\ N\end{smallmatrix}} (1 - \frac{\alpha}{2})}$ |
| 20.0 | 0.475 | 22.0 | 0.672 | 0.004 | 0.0227 | |
| 37.5 | 0.488 | 15.0 | 0.995 | 0.012 | 0.0200 | |
| 30.0 | 0.616 | 20.2 | 0.899 | 0.008 | 0.0158 | |
| 30.0 | 0.615 | 38.0 | 0.482 | 0.011 | 0.0160 | |

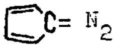
* V = 75.0 $cm^3$; t = 20°C; **for isotopic dilution, V and t see*

The isotopic analysis of diazirine undecomposed which was separated from irradiation products shows an original content of $N_2^{15}$, i.e. diazirine is not formed here from $CH_2$ and $N_2^{15}$. It is the same with diazomethane photolysis. Thus, the only product of reaction between methylene and nitrogen is diazomethane, $CH_2{<}\overset{N}{\underset{N}{\|}} \nleftarrow CH_2 + N_2 \rightarrow CH_2 = \overset{+}{N} = \overset{-}{N}$. The formation of diazomethane in diazirine photolysis in the gas phase was also observed by Amrich and Bell(8) who ascribed this to the isomerization of diazirine. However Moore and Pimentel(1) have shown that in a solid nitrogen matrix diazomethane is the product of reaction of $CH_2$ with $N_2$.

As seen from TABLE 1, the highest yield of $CH_2N_2^{15}$ can be obtained in the photolysis of diazomethane, the yield in case of diazirine being lower. This is probably due to the lower excess energy in methylene obtained from diazirine. As the methylene from ketene is nearly as active as $CH_2$ from diazirine, and the reaction of $CH_2$ with ketene is slower than that of $CH_2$ with diazirine, $f(CH_2CO)$ may be expected to be nearly the same as $f(CH_2{<}\overset{N}{\underset{N}{\|}})$. In fact, $f(CH_2CO)$ is almost ten times as small as $f(CH_2{<}\overset{N}{\underset{N}{\|}})$. This is presumably due to the instability of diazomethane in the presence of ketene. Indeed it was found experimentally that thermal decomposition of diazomethane is accelerated if some of ketene is added. In the case of phenylcyclopropane photolysis we could not accurately calculate f either, as degree of decomposition was determined only approximately to be less than 0.1. Maximum yield of $CH_2N_2^{15}$, 0.07% as related to initial phenylcyclopropane was obtained when irradiation time was 5 to 15 min in a silica vessel and the yield went down on further irradiation. This low yield can be explained at least partially by fast photolysis of the diazomethane formed in the experimental conditions.

The photolyses of several diazocompounds in $N_2^{15}$ have been studied in order to compare the reactivities of various carbenes towards nitrogen. The experiments were performed in pyrex and silica vessels at a pressure of $N_2^{15}$ 620 to 660 mm Hg (TABLE 3). It can be seen that the majority of substituted carbenes do not react with $N_2$. The only exceptions are $CF_3CH$: and (CN)CH: . For these two carbenes, an isotopic analysis shows an increased $N_2^{15}$ content in the diazocompounds, f value being less than one tenth of $f(CH_2N_2)$.

TABLE 3

| Source of carbene | $f\cdot 10^3$ | Source of carbene | $f\cdot 10^3$ |
|---|---|---|---|
| $CH_2N_2$ | 85 | $CH_2 = CHCHN_2$ | 0 |
| $CH_3CHN_2$ | 0 |  | < 0.1 |
| $CH_3CH_2CHN_2$ | 0 | $C_2H_5OCOCHN_2$ | < 0.1 |
| $CF_3CHN_2$ | 5 | $(CN)CHN_2$ | 3 |

Lack of reaction between ethylidene and $N_2$ can be explained by intramolecular rearrangement $CH_3CH: \longrightarrow CH_2 = CH_2$ which is apparently considerably faster than bimolecular reaction with $N_2$. No reaction of ethylidene with CO was observed either (9). Corresponding rearrangement of $CF_3CH:$ is much slower (10), therefore the reaction of the latter with $N_2$ is possible.

Absence of noticeable reaction of $N_2$ with $C_2H_5OCOCH:$ and $C_5H_4:$ shows that their reactivity is much lower than that of $CH_2$ as no rearrangement is known for these two carbenes (7a).

## REFERENCES

1. C.B.Moore, G.C.Pimentel. J.Chem.Phys. 41, 3504 (1964)

2a. Y.G.Borod'ko, A.E.Shilov, A.A.Shteinman. Dokl.Akad.Nauk SSSR, 168, 581 (1966)

b. L.N.Lobova, M.B.Tjabin, A.E.Shilov, A.A.Shteinman in "Mechanisms of respiration, photosynthesis and fixation of nitrogen", Nauka, Moskva (1967), p.335

c. A.A.Shteinman. Zh.Fiz.Khim. (in press)

3. W.Braun, J.R.McNesby, A.M.Bass. J.Chem.Phys., 46, 2071 (1967)

4. N.G.Moll, W.E.Thompson. J.Chem.Phys., 44, 2684 (1966)

5. W.B.De More, O.F.Raper. J.Chem.Phys. 37, 2048 (1962); Canad.J.Chem., 41, 808 (1963)

6. T.B.Wilson, G.B.Kistiakowsky. J.Am.Chem.Soc., 80, 2934 (1958)

7a. W.Kirmse. Carbene chemistry. N.Y.-L., 1964.

b. D.B.Richardson, L.R.Durret, J.M.Martin, W.E.Putman, S.C.Sloumacher, J.Dvoretzky. J.Am.Chem.Soc., 87, 2763 (1965)

8. M.I.Amrich, I.A.Bell. J.Am.Chem.Soc., 86, 292 (1964)

9. F.O.Rice, A.L.Glasebrook. J.Am.Chem.Soc, 56, 741 (1934)

10. R.Fields, R.N.Haszeldine. Proc.Chem.Soc., 22 (1960)