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REACTIONS OF ATOMIC CARBON WITH π-BONDED INORGANIC MOLECULES†

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Abstract—Atomic carbon (^{11}C) produced by nuclear transformations has been reacted with O_2, CO, CO_2, SO_2, N_2, N_2O, NO, and NO_2. With O_2, CO, CO_2, and SO_2, ^{11}CO is the only significant product. This is true even in liquid oxygen where there is no three-body restriction on CO_2 formation. These findings suggest that the dominant mode of attack is "end-on" rather than by the usual "sideways π-complex" mode. An examination of the molecular orbitals involved indicates that this should in general be the preferred mechanism of carbon atom attack on π-bonded inorganic molecules. With N_2, N_2O, and NO the carbon atom can form a strong bond at either end of the molecule. In accordance with this both ^{11}CO and ^{11}CN are observed as major products. With NO_2, ^{11}CO is the major product, again as required by the "end-on" attack mechanism.

These reactions occur with both hot and thermalized carbon atoms. Thus both hot and thermal ^{11}C can undergo the exoergic reactions with O_2 to form ^{11}CO and with N_2O to give ^{11}CO and ^{11}CN. By contrast the endoergic process in which ^{11}C combines with N_2 to form ^{11}CN occurs only with hot atoms.

ONLY a few studies of the reactions of carbon atoms with simple inorganic molecules have been reported. ROWLAND and LIBBY(1) used ^{11}C to investigate the reactions of carbon atoms with liquid and solid CO_2. ^{14}C has been used to study the reactions of carbon atoms with air.(2) The ammonia system has been investigated using both ^{14}C(3) and ^{11}C.(4,5) A preliminary survey of the reactions of ^{11}C with various gaseous oxides and with hydrogen has also appeared.(4,6) These studies have shown that in many oxygenated systems ^{11}CO tends to be the major product. The consequences of this finding for the reactions of natural ^{14}C have been investigated.(2,7) However, no proposals regarding the mechanism of the reactions of carbon atoms in gaseous inorganic systems have yet appeared.

A considerable body of evidence has recently appeared which shows that carbon

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† Abstracted in part from the Ph.D. thesis of M. L. Pandow, Yale University, 1960.

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(1) F. S. ROWLAND and W. F. LIBBY, *J. Chem. Phys.* **21,** 1493 (1953).

(2) M. PANDOW, C. MACKAY and R. WOLFGANG, *J. Inorg. Nucl. Chem.* **14,** 153 (1960).

(3) J. Y. YANG and A. P. WOLF, *J. Amer. Chem. Soc.* **82,** 4488 (1960).

(4) C. MACKAY, M. PANDOW, P. POLAK, and R. WOLFGANG in *Chemical Effects of Nuclear Transformations*, Vol. 2, p. 38. I.A.E.A. Vienna (1961).

(5) F. CACACE and A. P. WOLF, *J. Amer. Chem. Soc.* **82,** 3202 (1962).

(6) In addition to the references already given to the use of ^{11}C to study the reactions of C atoms with simple inorganic molecules some work has been done using this isotope to study carbon atom reactions in salts. See for example L. S. SHARMAN and K. J. MACCALLUM, *J. Amer. Chem. Soc.* **77,** 2989 (1955); W. J. EDWARDS and K. J. MACCALLUM, *Canad. J. Chem.* **34,** 189 (1956); and K. J. MACCALLUM and W. J. EDWARDS in *Chemical Effects of Nuclear Transformations*, Vol. 2, p. 57. I.A.E.A., Vienna (1961).

(7) C. MACKAY, M. PANDOW and R. WOLFGANG, *J. Geophys. Res.* **68,** 3929 (1963).

atoms insert into the π-bonds of alkenes.(8,9,10) Such reactions have also been observed for CH_2, C_2O, O and S.(11–14) Hence it is of particular interest whether a parallel reaction occurs between C atoms and inorganic π-bonded molecules. An investigation of this point is hampered by the fact that these systems are so simple as to present relatively few experimental variables. This bars many of the techniques, such as the use of degradations(9) and isotope tracers(10) which have been invaluable in investigation of the organic systems. Nevertheless the results obtained suggest a relatively clear answer.

EXPERIMENTAL

Irradiation

The ^{11}C was produced through the use of either the Yale Heavy Ion or Electron Accelerators.

The Heavy Ion Accelerator produces a pulsed 120 Mev ^{12}C ion beam. The target chamber (Fig. 1)† is attached to the end of the accelerator and the ^{12}C beam is focused on a 50 mg Pt–Au foil.

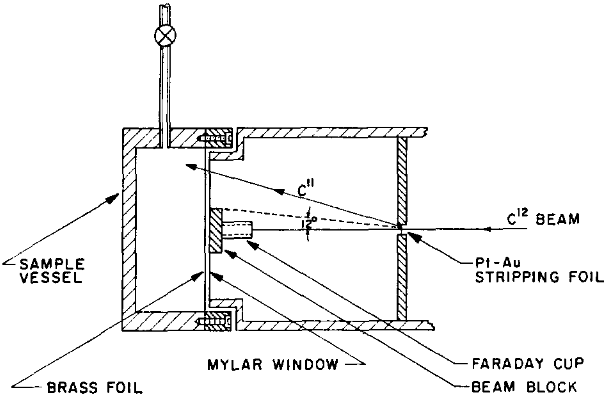

Fig. 1.—Hot atom target chamber.

Carbon-11 is produced by a neutron stripping reaction.[16] The ^{11}C retains most of the velocity of the incident ^{12}C, but is inelastically scattered away from the axis of the main beam.[17] Such scattered ^{11}C (Fig. 1) will pass through a 1 mil mylar window and a thin foil which forms one wall of the sample container. A part of the entering ^{11}C will be stopped by the reagent contained in the vessel.

The beam block bars the undeflected, main ^{12}C beam and most of the Rutherford scattered ^{12}C particles from entering the sample container. Since only a small fraction of the ^{12}C is scattered at angles greater than 12 degrees while the ^{11}C angular distribution peaks between 15 and 20 degrees,(17) this arrangement represents an optimum compromise between maximum ^{11}C delivery to the sample and minimum radiation damage primarily induced by the scattered ^{12}C.

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† This design is a slight modification of that previously described.(15)

(8) C. MacKay, P. Polak, H. E. Rosenberg and R. Wolfgang, *J. Amer. Chem. Soc.* **84**, 308 (1962).

(9) a. M. Marshall, R. Wolfgang and C. MacKay, *Tetrahedron Letters* **29**, 2033 (1963).
b. M. Marshall, C. MacKay and R. Wolfgang, *J. Amer. Chem. Soc.* (in press).

(10) J. Dubrin, C. MacKay and R. Wolfgang, *J. Amer. Chem. Soc.* **86**, 959 (1964).

(11) Much work has been done on the reactions of methylene radicals. See for example, W. Doering, R. G. Buttery, R. G. Loughlin and N. Chaudhuri, *J. Amer. Chem. Soc.* **78**, 3224 (1956).

(12) K. Bayes, *J. Amer. Chem. Soc.* **83**, 3712 (1961), and *J. Amer. Chem. Soc.* **84**, 4077 (1962); R. T. Mullen and A. P. Wolf, *J. Amer. Chem. Soc.* **84**, 3214 (1962).

(13) R. J. Cvetanovic, *Canad. J. Chem.*, **36**, 623 (1958); and *J. Chem. Phys.* **30**, 19 (1959).

(14) O. P. Strausz and H. E. Gunning, *J. Amer. Chem. Soc.* **84**, 4080 (1962).

(15) C. MacKay and R. Wolfgang, *Radiochim. Acta.* **1**, 42 (1962).

(16) R. Kaufmann and R. Wolfgang, *Phys. Rev.* **121**, 192 (1961).

(17) R. Kaufmann and R. Wolfgang, *Phys. Rev.* **121**, 206 (1961).

The Faraday cup serves as a monitor for the ^{12}C beam. The output from this cup is displayed on an oscilloscope as an aid in focusing the main beam on the stripping foil. The output signal is also fed to a modified ion chamber. This device acts as an integrator and gives a measure of the total ^{12}C and hence ^{11}C during a given irradiation.

For irradiation at the Yale Electron Linear Accelerator a 40–50 MeV Bremsstrahlung beam produced in an aluminium target was used. ^{11}C was created in carbon containing samples by a (γ, n) process and to a lesser extent in nitrogen containing samples by a $(\gamma, p2n)$ process. The peak energy (40–50 MeV) is considerably higher than the threshold ($\sim$20 MeV) of the (γ, n) process. This is advantageous since there is then a relatively larger number of high energy γ-rays which lead to the formation of ^{11}C and a smaller number of low energy γ-rays which can only promote radiation damage.

Radiation dosage

The radiation dosages to which these samples were subjected were estimated using benzene production from acetylene as a crude dosimeter.(18) The total radiation dose delivered to the sample, at either accelerator, was 10^{-2} eV/molecule or less under normal irradiation conditions.

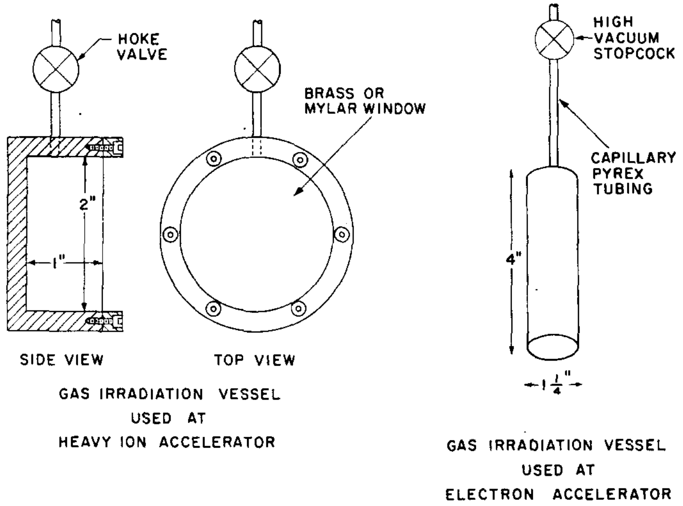

FIG. 2.—Irradiation vessels.

In addition, radiation oxidation of ^{11}CO to $^{11}CO_2$ was directly measured in all samples. Known quantities ($\sim$1 per cent) of inactive CO were added to the samples prior to irradiation. After irradiation the amount of CO_2 formed by radiation oxidation was measured by gas chromatography (see Analysis). The fraction of $^{11}CO_2$ which arose from radiation oxidation could then be estimated.

Isotopic purity of ^{11}C

Isotopic purity of the ^{11}C in O_2, CO, and CO_2 Heavy Ion Accelerator irradiations was established by half-life determinations using a metal internal gas counter and P-10 as a counting gas.(19) In electron accelerator runs sufficient time was allowed to elapse so that any 2 min O^{15} was a minor contaminant. Whenever nitrogen containing samples were irradiated some 10·0 min ^{13}N was formed. The ^{13}N activity appeared primarily as N_2 and N_2O and was separated by gas chromatography. (See ANALYSIS.)

Irradiation vessels

For heavy ion accelerator irradiations, sample containers shown in Fig. 2 were used. These vessels were fabricated from brass or stainless steel. In certain cases gold-plated, brass vessels were

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(18) F. W. LAMPE, *J. Amer. Chem. Soc.* **79**, 1055 (1957).

(19) R. WOLFGANG and C. MACKAY, *Nucleonics* **16**, 10, 69 (1958).

used. A 0·55 mil brass foil served as the irradiation window for the brass catchers; a 1 mil Mylar window was used with the stainless steel vessels.

For electron accelerator irradiations, Pyrex sample vessels also shown in Fig. 2 were used.

For irradiations of liquids, vessels of similar design but of considerably lower internal volume were used.

Reagents

The gases used as reactants were obtained from the Matheson Company and were of very high purity. Small amounts of air in nitrous oxide were removed by vacuum-line distillation. Nitrogen dioxide was synthesized from nitric oxide and oxygen. Gas chromatography of these gases indicated an impurity level of less than 0·2 per cent.

Certain carrier gases were synthesized. Carbon suboxide was prepared by dehydrating malonic acid. Hydrogen cyanide was made by treating sodium cyanide with sulphuric acid.

Analysis

After irradiation (~15 mins), the samples were expanded into four transfer vessels. Analyses were performed by means of gas chromatography using a window flow proportional counter in series with a standard thermistor detector so that mass and activity analyses could be performed simultaneously.(19,20)

Two different columns were used for the analysis of each sample. The *total volatile activity* of the sample was determined by passing two aliquots directly through the two associated counters. Two additional aliquots were then run through the two chromatographic columns.

A variety of chromatographic column fillings were used. CO and CO_2 were separated on two and five foot silica gel columns and on a 25 foot column consisting of 50 g of dimethylformamide on 100 gs of firebrick. The latter column also separated out a small amount of ^{13}N labeled N_2O formed in N_2, NO_2, and N_2O runs. A 2 ft, 5A molecular sieve and 5 ft charcoal column were used to separate ^{11}C and $^{13}N_2$ formed in N_2, NO and N_2O runs. Whenever adsorption columns were used, carrier quantities of ^{12}CO and $^{12}CO_2$ were added to the sample subsequent to the irradiation to eliminate any irreversible adsorption of trace ^{11}CO and $^{11}CO_2$. COS was determined on a 2 ft silica gel column. Carbon suboxide was separated on a 30% G.E. SF 96 column on firebrick.

Identification of CN *radical*

The presence of the cyanide radical in certain samples was established by using ethylene as a radical scavenger.† Hydrogen cyanide and acrylonitrile were identified as the scavenged products. No propionitrile was found outside the limits of detection (~1 per cent). Higher nitriles were not sought.

Since trace ^{11}HCN was complexed by the brass or stainless steel vessels, small carrier amounts ($\leq$0·2 per cent) of inactive HCN had to be added to the samples prior to the irradiation in order to recover the ^{11}HCN. Similar quantities of inactive acrylonitrile were sometimes added in order to be certain that the bulk of the labeled nitrile formed was recovered.

Acrylonitrile was separated on a 10 ft column consisting of 3 per cent of 1,2,3-tris(2-cyanoethoxy) propane on Anakrom ABS and transferred to and confirmed on a 10 foot 30% G.E. SF 96 column on firebrick. Hydrogen cyanide was also separated on the 1,2,3-tris(2-cyanoethoxy) propane column.

Monitoring

In heavy ion accelerator irradiations the actual number of ^{11}C stopped by the reagent in the sample container is a function of the stopping power of this reagent. The stopping power is related to the atomic numbers of the component atoms of the reagent.

In order to establish absolute yields we have used O_2 as a monitor. An O_2 sample containing a pressure of oxygen adjusted to have the same stopping power‡ as the sample is irradiated for the same

† It has been reported that CN reacts very rapidly with ethylene. No product identifications were made.(21)

‡ Relative atomic stopping powers have been calculated using the range-energy data of MARTIN and NORTHCLIFFE.(22)

(20) R. WOLFGANG and F. S. ROWLAND, *Analyt. Chem.* **30**, 903 (1958).

(21) D. E. PAUL and F. W. DALBY, *J. Chem. Phys.* **37**, 592 (1962).

(22) F. W. MARTIN and L. C. NORTHCLIFFE, *Phys. Rev.* **128**, 1166 (1962).

period and under similar beam conditions as the sample. After normalization to equal integrated beam intensities the total volatile ^{11}C activity in the O_2 is taken to be equal to the number of ^{11}C atoms reacting in the sample. Absolute yields are then calculated by dividing the total activity in the oxygen monitor into the observed activity of any given product.

This technique assumes that all of the ^{11}C reacts in O_2 to give ^{11}CO (and possibly $^{11}CO_2$). This is confirmed by the observation that total sample activities monitored this way never exceed but often equal 100 per cent. Furthermore yields in ethane calculated on this basis are in agreement with results from a different laboratory(23) in which absolute yields were measured by a more direct method.

In electron accelerator irradiations, the yield of ^{11}C is directly proportional to the number of ^{12}C atoms in the sample (relative differences in recoil losses are usually negligible). Monitoring is accomplished by simultaneously irradiating two separately filled samples, one of whose absolute recovery has been previously determined. Both samples are rotated on a turntable such that each receives equal exposure to the beam. The samples can then be intercompared as described above.

Yields

Yields of various products can be computed as per cent of *total volatile activity* or per cent of *expected activity*. The former is arrived at by comparing the activity of a specific peak with the total volatile activity. The latter is computed by comparing the activity of a specific peak with the total activity ($^{11}CO + {}^{11}CO_2$) of an oxygen monitor. The total volatile activity can also be directly compared to the oxygen monitor.

RESULTS

Results of this work are summarized in Tables 1, 2, and 3. Table 1 reports the results of the reaction of carbon atoms with O_2, CO, CO_2, and SO_2. The only important product found is ^{11}CO which accounts for more than 95 per cent of the ^{11}C activity in every reaction.

TABLE 1.—PRODUCTS OF REACTIONS OF ^{11}C ATOMS WITH OXYGEN AND SOME OTHER GASEOUS OXIDES

Principal reactant	Composition of reaction mixture (cm Hg.)				
	Principal reactant	Ne	CO	CO_2	$^{11}CO^a$ (%)
O_2	75·0		0·6	0·6	97·0
O_2	Liquid				99·7
O_2	1·0	75·0	0·01	0·01	98·7
CO	75·0			0·8	95·0[b]
CO_2	75·0		0·8		98·0
SO_2	75·0		0·3	0·3	97·5[c]

[a] Individual results are the average of several runs. Other product is $^{11}CO_2$ unless otherwise indicated. Yields are per cent total volatile activity which corresponds $\geq$ 90 per cent of the total activity on the basis of an O_2 monitor.

[b] With CO a yield of C_3O_2 varying between 2 and 4 per cent is found.

[c] With SO_2 a 0·5 per cent yield of SCO is found when SCO carrier is present.

The results of the reaction of ^{11}C atoms with N_2 and with the various oxides of nitrogen are given in Table 2. For all runs, yields are reported as percent of total activity. The cyanide radical was identified through its reaction with ethylene scavenger to give hydrogen cyanide and acrylonitrile. (See EXPERIMENTAL.) Since C atoms react efficiently with ethylene(8,9,10) substantial yields of hydrocarbons are also found in experiments in which this scavenger was present. Since these were not relevant to

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(23) G. STOCKLIN and A. P. WOLF, *J. Amer. Chem. Soc.* **85**, 229 (1963).

this inquiry they were not always determined. They presumably account for a large fraction of the "missing" activity in experiments such as those with NO_2 (last entry in Table 2).

DISCUSSION

Kinetic energy of ^{11}C

The ^{11}C is initially produced at kinetic energies ($\sim 10^{5-8}$ eV) which are essentially infinite on the chemical energy scale. At these energies the ^{11}C cannot undergo stable chemical combination. Instead a large fraction of its energy will be dissipated in collisions with the target material.

Table 2.—The reactions of ^{11}C atoms with N_2 and with oxides of nitrogen

Composition of reaction mixture (cm Hg.)				Yields[a]		
Principal reactant	Principal reactant	C_2H_4	Ne	^{11}CO	Recovered cyanide[b]	Hydrocarbons
N_2	77·2	1·7		1·4	21	21
N_2	1·9	0·04	75·4	35[c]	3	12
N_2O	77·5			67	None	None
N_2O	75·8	1·2		34	40	2
N_2O	1·9	0·04	75·4	53	35	2
NO	75·0			60	None	None
NO	75·6	1·4		56	4	N.D.
NO	41·6	35·4		30	8	21
$NO_2(N_2O_4)$	74·5			81	None	None
$NO_2(N_2O_4)$	40	38		24	≤ 3	N.D.

[a] Yields are per cent total activity, based on an O_2 monitor. The presumed reason for the lower recovery in the absence of C_2H_4 is reaction of CN at the vessel walls. The entry N.D. means not determined.

[b] Cyanide is recovered as acrylonitrile and HCN except in the case of NO_2 where HCN could only be measured.

[c] Result of reaction with O_2 impurity.

Table 3.—Effect of moderation in cyanide yields in N_2 and N_2O systems

System	Product	Yields[a]	
		Unmoderated	Moderated by 95% neon
N_2—C_2H_4	Cyanide	21	3
N_2O—C_2H_4	Cyanide	40	35

[a] Yields are per cent total activity on basis of an O_2 monitor.

When the energy of the ^{11}C is somewhere below 100 eV chemical combination can take place. In this energy region the ^{11}C is expected to be a neutral atom in its ground (^3P) or a low lying excited (^1D or ^1S) electronic state.† The ^{11}C atom can react while it has excess kinetic energy ("hot reaction") or at thermal kinetic energies. The "hot" ^{11}C can undergo chemical reactions involving very high activation energies. If a large excess of an inert moderator, such as neon, is added to a system the probability that a ^{11}C will suffer a high energy collision with a reactant molecule is greatly reduced.

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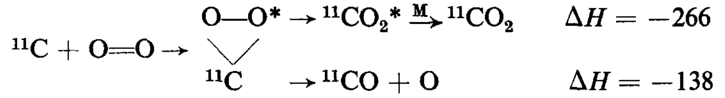
† This is discussed in detail in Reference (9b).

Hence the yield of a product derived from a hot process will similarly be reduced, while those resulting from thermal reactions will be enhanced. Thus it is possible to distinguish hot and thermal reactions, if they lead to different products.[24]

Proposed mechanisms: π-bond and end-on attack

A priori, two models for attack of a C atom on inorganic molecules seem plausible. The first involves attack at the π-bond to form a cyclic intermediate (I). This intermediate can either rearrange to CO_2^* or decompose directly to CO and O.



$$ {}^{11}\mathrm{C} + \mathrm{O{=}O} \rightarrow \begin{array}{l} \mathrm{O{-}O^*} \rightarrow {}^{11}\mathrm{CO_2}^* \xrightarrow{M} {}^{11}\mathrm{CO_2} \qquad \Delta H = -266 \\ \diagdown\diagup \\ {}^{11}\mathrm{C} \qquad \rightarrow {}^{11}\mathrm{CO} + \mathrm{O} \qquad \Delta H = -138 \end{array} \qquad (1) $$

(The energetics of the above and following reactions are calculated for ground state (^3P) carbon atoms.)

This mode of attack has previously been suggested as important in the reaction of carbon atoms with ethylene.[8,9,10] In the gas phase at ordinary pressures the decomposition of CO_2^* is expected. However, in the liquid phase some de-excitation and stabilization as CO_2 seems reasonable.†

The second possible mode of attack involves an "end-on" approach by the carbon atom to form a linear C—O—O intermediate. (Equation 2.) Such an intermediate

$$ {}^{11}\mathrm{C} + \mathrm{O{=}O} \rightarrow {}^{11}\mathrm{C{-}O{-}O^*} \rightarrow {}^{11}\mathrm{CO} + \mathrm{O} \qquad \Delta H = -138 \qquad (2) $$

can decompose to CO but formation of CO_2 is unlikely, even in the condensed phase.

Failure to observe CO_2 formation in the reaction of C atoms with liquid oxygen indicates that the "end-on" attack mechanism is dominant. This reaction mode also provides a more consistent explanation of all our other results in inorganic systems.

Basis of the preference for end-on attack

There also appear to be good theoretical reasons why "end-on" attack should be important in the carbon atom-oxygen system. Consider, as an example, the reaction of a C(^3P) atom with oxygen. Fig. 3 shows conventional diagrams of the p atomic orbitals of the carbon atom and of the oxygen anti-bonding molecular orbitals. It is clear from these diagrams that approach of a carbon atom along the O—O bond axis in oxygen can lead to a particularly favourable situation for the establishment of a strong chemical bond involving these orbitals. The empty $2p_x$ orbital of carbon is in a favourable position to interact with the occupied $\sigma(2s)^*$ orbital of oxygen. Furthermore, the singly occupied $2p_y$ and $2p_z$ orbitals of the carbon atom

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† If the CO_2^* were formed directly by the reaction of a carbon atom with oxygen it would have an internal energy of at least 266 kcal depending on the energy brought to the reaction complex by the carbon atom. However a large part of this energy could be dissipated before the cyclic complex isomerizes to CO_2. Thus the CO_2^* may contain considerably less energy than 266 kcal when formed. Very little is known of the lifetimes of small, highly excited complexes. However, in the liquid phase survival of CO_2 seems reasonable. The bases of this expectation are the known high efficiencies of collisional energy transfer from highly excited systems[25] and the well known Franck-Rabinovitch "cage-effect" which can promote recombination of dissociated fragments provided they are in appropriate geometrical configurations.

[24] P. J. ESTRUP and R. WOLFGANG, *J. Amer. Chem. Soc*, **82**, 2061 (1961).

[25] J. W. SIMONS and B. S. RABINOVITCH, *J. Amer. Chem. Soc.* **85**, 1023 (1963).

can interact with the singly occupied π_y* and π_z* orbitals of oxygen. Thus the unfavourable transfer of electron density from oxygen to carbon associated with the first mode of interaction is effectively compensated by a transfer in the other direction due to the second mode. This is a synergic effect of the type postulated by Orgel(26) as an explanation of the stability of the carbonyl compounds of the transition metals. It leads to the formation of a bond analogous to the C—O bond in carbon monoxide, one of the strongest of chemical bonds.

In contrast, consideration of a possible π-complex between a carbon atom and oxygen indicates that it should be somewhat weaker than that between a carbon atom and ethylene. The strength of a π-complex must in part be a function of the electron affinity of the acceptor (in this instance carbon), and the ionization potential of the donor. The ionization potential of ethylene is 11·3 eV(27) and that of O_2 is 12·2 eV,(27) indicating that oxygen should be a poorer donor of electrons in "sideways", π-bond formation. In view of these considerations, it is not surprising that in oxygen "end-on" attack seems more favoured over "sideways" attack on the π-bond.(8,9,10) (Conversely in ethylenic systems these factors, and also interference with "end-on" attack by terminal hydrogen atoms (or alkyl groups), makes a "sideways" attack the favoured mode.)

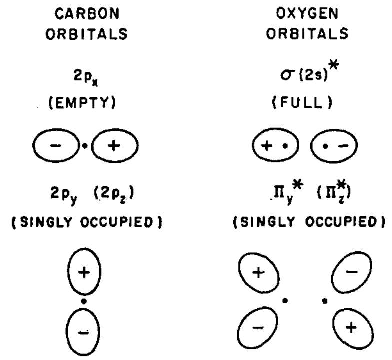

FIG. 3.—Orbitals available for bonding in C and in O_2.

Similar considerations indicate that the "end-on" attack mechanism should be dominant in the reactions of a C(^3P) atom with other π-bonded inorganic oxides. Furthermore, this mechanism should be important in the reactions of electronically analogous systems which involve atoms such as C(^1D) and N(^4S).

Effect of moderator on $^{11}C + O_2$ *system*

In the presence of excess moderator most carbon atoms cannot react until they reach thermal energies. As shown in Table 1, this does not change the result that nearly all of them react to form ^{11}CO. The indicated low activation energy for this reaction is consistent with its highly exoergic nature.

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(26) L. E. ORGEL, *An Introduction to Transition Metal Chemistry: Ligand Field Theory*, p. 135. Methuen, London (1960).

(27) R. W. KISER, *Tables of Ionization Potentials*, U.S. A.E.C., Office of Technical Information (1960).

The reactions with CO, CO_2, *and* SO_2

There are three products possible from the reaction of ^{11}C with CO. These are shown in Reactions (3), (4), and (5).

$$^{11}C + CO \rightarrow {}^{11}COC \rightarrow {}^{11}CO + C \qquad \Delta H = 0 \qquad (3)$$

$$^{11}C + CO \rightarrow {}^{11}CCO \qquad \Delta H = -82^{(28)} \qquad (4)$$

$$^{11}C + CO \rightarrow {}^{11}CCO \rightarrow {}^{11}CC + O \qquad \Delta H = +148 \qquad (5)$$

Formation of C_2 is possible only with hot atoms. There is no evidence that it is formed in any significant yield. The third body requirement on the formation of C_2O makes a significant yield of this product unlikely in the presence of an efficient competing reaction.† As expected there are no restrictions on the formation of ^{11}CO which is the only important product formed.

Similarly ^{11}C reacts with CO_2 and SO_2 to yield only ^{11}CO as a major product. The possible reactions with CO_2 and SO_2 are: (These reactions are written in compliance with the spin conservation rule.)

$$^{11}C + CO_2 \rightarrow {}^{11}CO + CO(^3\Sigma) \qquad \Delta H = +8 \qquad (6)$$

$$^{11}C + CO_2 \rightarrow {}^{11}CO_2 + C \qquad \Delta H = 0 \qquad (7)$$

$$^{11}C + CO_2 \rightarrow {}^{11}C_2O + O \qquad \Delta H = +45 \qquad (8)$$

$$^{11}C + SO_2 \rightarrow CO + SO \qquad \Delta H = -108 \qquad (9)$$

$$^{11}C + SO_2 \rightarrow CO_2 + S \qquad \Delta H = -142 \qquad (10)$$

$$^{11}C + SO_2 \rightarrow SCO + O \qquad \Delta H = -75 \qquad (11)$$

It is significant that SCO, which would be expected to result from a "sideways" π-bond insertion of C into the OS bond is found in no more than 0·5 per cent yield.

The reaction with nitrogen

With N_2 the end-on attack mechanism should also be operative. The expected product, the CN radical, is observed. The reaction leading to the CN radical is endothermic for both $C(^3P)$ and $C(^1D)$ atoms.‡

$$C(^3P) + N_2(^1\Sigma) \rightarrow CN(^2\Sigma) + N(^4S) \qquad \Delta H = +50 \qquad (12)$$

$$C(^1D) + N_2(^1\Sigma) \rightarrow CN(^2\Sigma) + N(^2D) \qquad \Delta H = +75 \qquad (13)$$

As Table 3 shows, the production of CN is nearly eliminated when the C atom is thermalized. This is consistent with the highly endoergic character of reactions (12) and (13). The results clearly show that (in the absence of moderator) carbon atoms can and do undergo hot reaction as required to form CN.

The reaction with N_2O

With N_2O, strong bonds can be formed by C atoms with either the N or O atoms of the molecule. Therefore both CN and CO are expected products.

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† Note that a small yield of C_3O_2, the product of the reaction of C_2O with CO was formed (Table 1).

‡ A value of $\Delta H_f = 109$ kcal was used for the $CN(^2\Sigma)$,(29) The reactions, involving CN formation, have been written in accordance with the spin conservation rule.

(28) The heat of formation of C_2O was estimated using the data of H. B. Palmer and T. J. Hirt, *J. Amer. Chem. Soc.* **84,** 113 (1962).

(29) J. Berkowitz, *J. Chem. Phys.* **36,** 2533 (1962).

$$C(^3P) + N_2O(^1\Sigma) \rightarrow CN(^2\Sigma) + NO(^2\pi) \qquad \Delta H = -60 \tag{14}$$
$$\rightarrow CO(^3\Sigma) + N_2(^1\Sigma) \qquad \Delta H = -79 \tag{15}$$
$$C(^1D) + N_2O(^1\Sigma) \rightarrow CN(^2\Sigma) + NO(^2\pi) \qquad \Delta H = -87 \tag{16}$$
$$\rightarrow CO(^1\Sigma) + N_2(^1\Sigma) \qquad \Delta H = -244 \tag{17}$$

Table 2 shows that both of these products are found in large yield. Since the reactions to produce the cyanide radical from N_2O are exoergic, thermalization of ^{11}C should not necessarily lead to the elimination of the CN yield. Table 3 shows that this expected behaviour is experimentally observed. Hence the carbon atom can react as either a hot or thermal species with N_2O to yield CN.

The N_2 and N_2O results indicate that the "end-on" mode of attack is important for both hot and thermal C atoms.

Reaction with NO

The "end-on" mechanism of attack would predict that both the CN and CO would be expected as products of the reaction of C atoms with NO.

$$C + NO \rightarrow CN + O \qquad \Delta H = -25 \tag{18}$$
$$C + NO \rightarrow CO + N \qquad \Delta H = -108 \tag{19}$$

Table 2 shows that both of these products are observed in agreement with the "end-on" mode of attack. The data on CN recovery suggest that the relatively low yields observed are due to reaction with NO by either the CN radical or its adduct with ethylene.†

Reaction with NO_2

The possible reactions of ^{11}C with NO_2 are listed below.

$$C + NO_2 \rightarrow CO + NO \qquad \Delta H = -185 \tag{20}$$
$$C + NO_2 \rightarrow CO_2 + N \qquad \Delta H = -162 \tag{21}$$
$$C + NO_2 \rightarrow CNO + O \tag{22}$$
$$C + NO_2 \rightarrow CN + 2O \qquad \Delta H = +46 \tag{23}$$

As expected from the "end-on" attack model, Table I shows ^{11}CO is the only important product.

SUMMARY

The reactions of carbon atoms with π-bonded inorganic oxides follow a relatively simple pattern. The ^{11}C reacts almost exclusively at the terminal orbitals rather than at the π-bonding orbitals. This is in marked contrast to alkene systems where "sideways" π-bond addition is very important. Both hot and thermal carbon atoms undergo this "end-on" mode of attack.

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† It has been observed that the CN radical reacts efficiently with NO.(30)

(30) N. BASCO, J. E. NICHOLAS, R. G. W. NORRISH and W. H. J. VICKERS, *Proc. Roy. Soc.*, A **272**, 147 (1963).