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Free Radicals by Mass Spectrometry. XXVII. Ionization Potentials of Four Pentyl Radicals

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Vertical ionization potentials of four pentyl radicals have been measured by electron impact on radicals generated by thermal decomposition of appropriate hexyl nitrites. The ionization potentials are: neo-pentyl 8.33, 3-pentyl 7.86, 2-pentyl 7.73 and *t*-pentyl 7.12 v. Using these values and thermochemical data, the ionic heats of formation are estimated to be 196, 187, 184 and 165 kcal./mole, respectively. Ionization potentials calculated by a semi-empirical group orbital method are in good agreement with the experimental values.

Introduction

In the present work four pentyl radicals have been produced by thermal decomposition of hexyl nitrites, and the vertical ionization potentials of the radicals have been measured by electron impact. This is a continuation of previous measurements of a similar kind for propyl and butyl radicals.[2]

Experimental

The apparatus and experimental procedures were essentially the same as those outlined in an earlier publication.[2] The pentyl radicals were obtained by thermal decomposition of the corresponding hexyl nitrites in a low pressure reactor, according to the reactions

$$C_5H_{11}CH_2ONO \longrightarrow C_5H_{11}CH_2O + NO$$
$$C_5H_{11}CH_2O \longrightarrow C_5H_{11} + CH_2O$$

The nitrites were prepared from the alcohols by reaction with sodium nitrite and dilute sulfuric acid.[3] In the case of the neopentyl radical, the corresponding alcohol 3,3-dimethyl 1-butanol was not commercially available. It was prepared from *t*-butylacetic acid by reaction with $LiAlH_4$.[4]

Attempts to produce the *n*-pentyl radical from *n*-hexyl nitrite were unsuccessful. No pentyl radicals could be detected at low electron energies at furnace temperatures from 300 to 500°. The formation of such products as ethyl radicals and propylene, and to a smaller extent propyl and methyl radicals and ethylene, indicated that the *n*-pentyl radicals dissociated as rapidly as they were formed.

Measurement of Ionization Potentials.—The method used in earlier work[2] for obtaining the ionization efficiency curves for the parent ion of a free radical is based on calculating a net peak height for the radical, using 50 v. electrons. This requires that all the products of the reaction be identified and that their contributions to the parent peak of the radical be subtracted as in the customary methods of mass spectrometric analysis. The logarithm of the radical ion current calculated as a percentage of the 50 v. value is then plotted against the electron accelerating potential and compared to a similar curve for the standard gas. For all the radicals examined so far, the curve for the radical is found to be parallel to the curve for the standard within ± 0.05 v. over the range from 0.1% to about 3% of the 50 v. value.[2] For the pentyl radicals, the reaction mixture was quite complex and a reliable value for the net radical peak height at 50 v. could not be calculated. Instead, a curve-matching procedure similar to that used by Foner and Hudson was employed.[5] This process consists, in effect, in moving the radical ionization efficiency curve vertically with respect to the standard curve (by multiplication by a suitable factor) until the difference in electron energy ΔV_e between corresponding points of the two curves is constant over the widest range. In view of the parallelity of radical and standard curves observed in the "50 V. normalization" method used earlier, these two methods should give the same ΔV_e. This was checked experimentally for a number of molecules, including the methyl radical. A comparison of the results given by the two procedures with each other and with spectroscopic and photoionization values is given in Table I. With the exception of methane, the differences between the two procedures are relatively minor. For methane, curve-matching gives an appreciably lower ionization potential than the 50 v. normalization, and one which is in better agreement with the photoionization value.

TABLE I

A COMPARISON OF IONIZATION POTENTIALS MEASURED BY VARIOUS METHODS

Compound	Reference gas	Obsd. ionization potential (volt) Photoionization or spectroscopy	50 volt normalization	Curve-matching
CH_4	Xe	12.98[a]	13.17[d]	12.94[d]
CO_2	Kr	13.79[a]	13.95[d]	13.88[d]
Xe	Kr	12.13[b]	12.01[d]	12.13[d]
Kr	Xe	14.00[b]	14.12[d]	14.02[d]
CH_3	Kr	9.85[c]	9.95[e]	9.95[d]

[a] K. Watanabe, T. Nakayama and J. Mottl, "Final Report on Ionization Potential of Molecules by a Photoionization Method," Dept. of Physics, University of Hawaii. 1959. [b] C. E. Moore, Natl. Bur. Standards Circ. No. 467 (1949). [c] G. Herzberg and J. Shoosmith, *Can. J. Phys.*, **34**, 523 (1956). [d] This work. [e] F. P. Lossing, K. U. Ingold and I. H. S. Henderson, *J. Chem. Phys.*, **22**, 621 (1954).

TABLE II

DETERMINATION OF I(3-PENTYL) BY CURVE MATCHING

(a)

Intensity [%]	V_e (Xenon) (volt)	V_e(Radical, m/e = 71) (volt) Assumed 50 volt radical intensity					
		10 cm.	20 cm.	30 cm.	40 cm.	60 cm.	80 cm.
3.0	13.89	9.25	9.50	9.69	9.85	10.13	10.39
1.0	13.48	8.91	9.12	9.25	9.35	9.50	9.64
0.3	13.11	8.56	8.76	8.89	8.96	9.09	9.18
0.1	12.80	..	..	8.56	8.65	8.76	8.84

(b)

Intensity [%]	$\Delta V_e = V_e$(Xenon) $- V_e$(Radical, m/e = 71) (volt) Assumed 50 volt radical intensity					
	10 cm.	20 cm.	30 cm.	40 cm.	60 cm.	80 cm.
3.0	4.64	4.39	4.20	4.04	3.76	3.50
1.0	4.57	4.36	4.23	4.13	3.98	3.84
0.3	4.55	4.35	4.23	4.14	4.02	3.93
0.1	..	..	4.24	4.15	4.04	3.96

An objective method for curve-matching is illustrated by reference to Tables II(a) and (b) and Fig. 1. The second column of Table II(a) gives the electron accelerating potentials at which the standard gas peak height is 3, 1, 0.3 and 0.1% of its 50 v. value. In the following columns the potentials are given at which the 3-pentyl radical peak height is the same percentage of various assumed 50 v. peak heights. These values are taken from the average of several indi-

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[1] National Research Council Postdoctorate Fellow 1959–1960.

[2] J. B. de Sousa and F. P. Lossing, *J. Am. Chem. Soc.*, **81**, 281 (1959).

[3] "Organic Syntheses," Vol. XVI, John Wiley and Sons, Inc., New York, N. Y., 1936.

[4] J. H. Hunter and J. A. Hogg, *J. Am. Chem. Soc.*, **71**, 1922 (1949).

[5] S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **25**, 602 (1956).

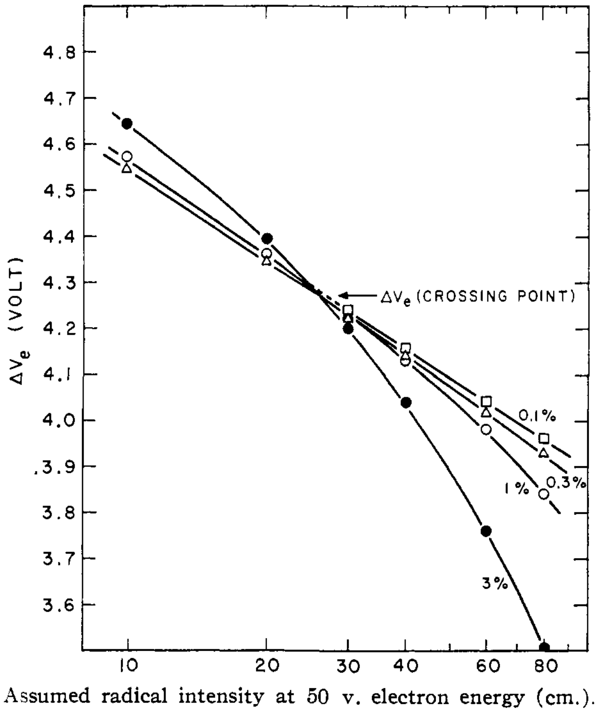

Fig. 1.—Graph showing the choice of the best value for the difference in ionization potential between the unknown and the standard gas, based on curve matching.

vidual ionization efficiency curves. Table II(b) gives values of ΔV_e taken from Table II(a). These are plotted, as in Fig. 1, to give a family of curves of ΔV_e *versus* the assumed 50 v. peak height. Ideally these four curves should have a common crossing point; the peak height at this point being the correct 50 v. peak height for the radical, and ΔV_e at this point being the correct voltage difference from the standard. In practice it is found that the four curves do not cross at exactly the same point, but there is a region in which they are all close together. The point of minimum spread, however, can be chosen quite objectively. In Fig. 1, the best value for ΔV_e lies quite clearly at $\Delta V_e = 4.27$ with an uncertainty of less than ± 0.05. The lack of an exact crossing point is partly due to the usual experimental uncertainty, and partly to the fact that, as a result of possible fine structure in the curves, the concept of parallelity is only an approximation.

Results and Discussion

The vertical ionization potentials of neopentyl, 2- and 3-pentyl and *t*-pentyl radicals, as measured by the curve-matching procedure, are given in Table III. The stated errors give approximately the uncertainty of determining the crossing points in the curves of the type given in Fig. 1. In an earlier paper[2] the experimental ionization potentials of propyl and butyl radicals were compared with values calculated by a semi-empirical group-orbital method, assuming planar configurations. In Fig. 2 an extension of this comparison is given, including values for the eight possible pentyl radicals calculated on the same basis. In general, with regard to the differentiation into primary, secondary and tertiary radicals, the agreement between the experimental and the calculated values is satisfactory. It follows, therefore, that in the decomposition of the alkyl nitrites so far studied no significant amount of rearrangement of primary or secondary radicals to the more stable isomers has occurred. In all cases except the 3-pentyl radical, the ionization potentials observed for pentyl radicals are a little lower than the calculated ones. The difference, however, probably is within the experimental uncertainty.

TABLE III

VERTICAL IONIZATION POTENTIALS AND ESTIMATED IONIC HEATS OF FORMATION OF PENTYL RADICALS

Radical	Ionization potential Volts	Ionization potential Kcal./mole	Estimated ΔH_f(ion) kcal./mole
Neopentyl	8.33 ± 0.1	192 ± 2	196
3-Pentyl	7.86 ± .05	181 ± 1	187
2-Pentyl	7.73 ± .1	178 ± 2	184
t-Pentyl	7.12 ± .1	164 ± 2	165

With the possible exception of *t*-pentyl, it is not possible to derive bond dissociation energies by combining the ionization potentials with the appearance potentials of pentyl ions from hydrocarbons. It seems quite clear from the work of Stevenson[6] that rearrangements to give the more stable secondary pentyl ions occur during dissociative ionization of *n*-alkanes. A rearrangement of a nominally secondary pentyl derivative to give a *t*-pentyl ion also cannot be ruled out. With neopentyl ion there is the further difficulty that this ion does not seem to be formed at all in dissociative ionization processes. As pointed out by Field and Franklin,[7] neopentyl ion once formed may isomerize rapidly into *t*-pentyl ion in the gas phase. This isomerization occurs with neopentyl chloride in the liquid phase in the presence of $AlCl_3$.[8] On account of these difficulties it would seem that the appearance potential data for primary and secondary pentyl ions are quite ambiguous. It is of interest, however, to combine the ionization potentials with estimates for the heats of formation of the radicals from kinetic data to arrive at estimated ionic heats of formation and to compare these with $\Delta H_f(C_5H_{11}^+)$ values from appearance potentials. Such comparisons may throw some light on the identity of ions produced in the dissociative ionization processes.

***t*-Pentyl.**—The bond dissociation energy D(*t*-butyl–H) appears to be established with reasonable certainty by both bromination kinetics and electron impact as 90 kcal./mole.[9] Assuming, as seems reasonable, that D(*t*-pentyl–H) is also 90 kcal./mole, and taking ΔH_f (isopentane) = −36.92 kcal./mole,[10] ΔH_f(*t*-pentyl) is 1.0 kcal./mole. Then from I(*t*-pentyl) = 7.12 v. we obtain ΔH_f(*t*-pentyl$^+$) = 165 kcal./mole. This agrees quite well with 161 kcal./mole estimated by Field and Franklin.[7] An upper limit for ΔH_f(*t*-pentyl$^+$) can also be obtained from the appearance potential of $C_5H_{11}^+$ ion in the dissociative ionization of 2,2-dimethylbutane

$$(CH_3)_3CC_2H_5 + e \longrightarrow (CH_3)_2\overset{+}{C}C_2H_5 + CH_3 + 2e$$

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[6] D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 867 (1953).

[7] F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957.

[8] P. D. Bartlett, F. E. Condon and A. Schneider, *J. Am. Chem. Soc.*, **66**, 1531 (1944).

[9] T. L. Cottrell "The Strengths of Chemical Bonds," 2nd Ed., Butterworths Scientific Publications, London, 1958.

[10] F. D. Rossini, *et al.*, "Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds," Carnegie Press, Pittsburgh, 1953.

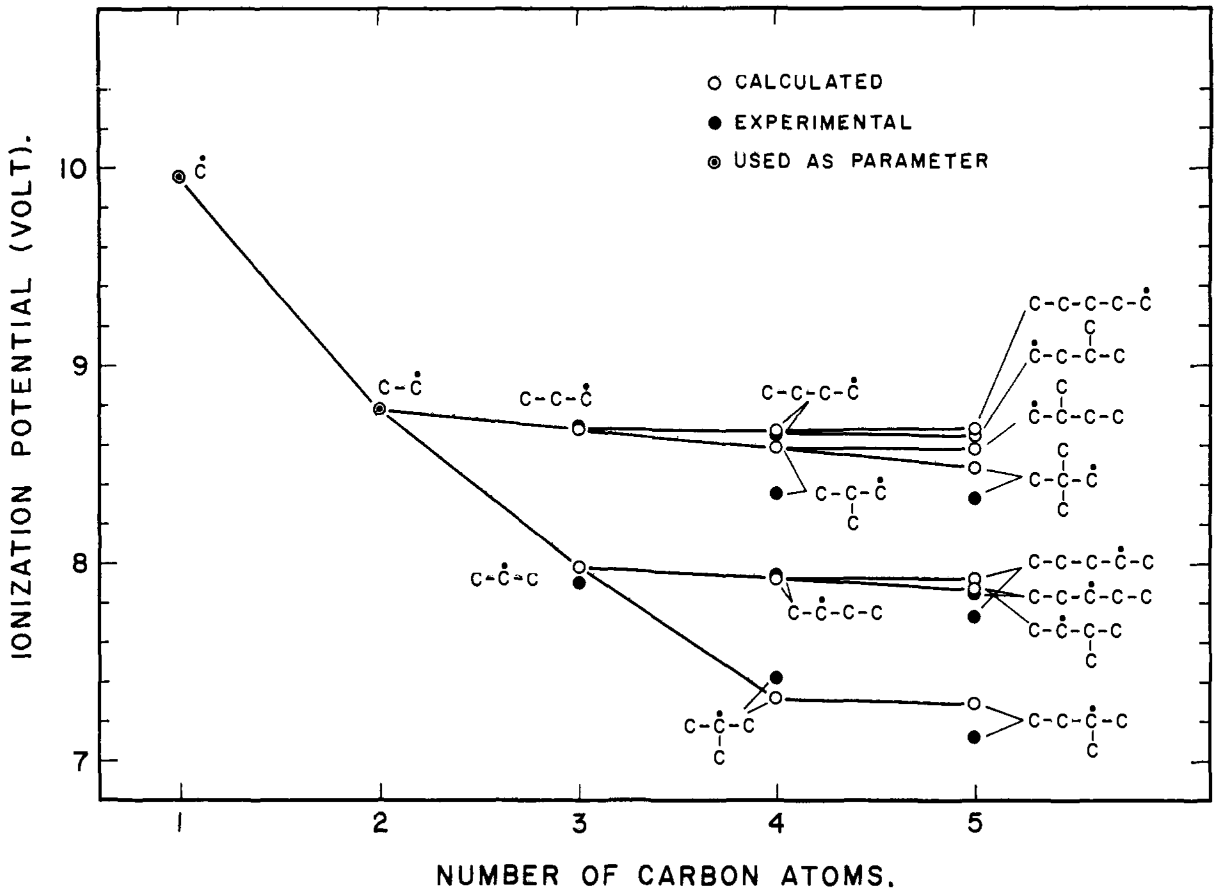
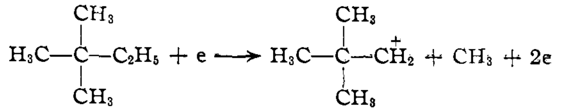


Fig. 2.—Comparison of calculated and experimentally measured vertical ionization potentials for C_1–C_5 alkyl radicals, showing a distinct separation into the three groups: primary, secondary and tertiary radicals.

We find this appearance potential, evaluated by the curve-matching procedure, to be 10.54 v. (evaluation of the curves by the vanishing-current method gave 10.58 v.). This is appreciably higher than that found by Koffel and Lad[11] who, however, used the linear extrapolation method shown since to be unreliable for fragment ions. Our appearance potential, combined with standard heats of formation,[10] gives $\Delta H_f(t\text{-pentyl}^+) \leq 167$ kcal./mole, in agreement with the value given above.

Neopentyl.—The bond dissociation energy D-(neopentyl-H) appears to be reliably established by bromination kinetics as 95.5 kcal/mole.[9,12] From this, and I(neopentyl) = 8.33 v., one obtains $\Delta H_f(\text{neopentyl}^+) = 196$ kcal./mole, in agreement with a prediction of 194 kcal./mole by Field and Franklin.[7] As mentioned above, no value for $\Delta H_f(\text{neopentyl}^+)$ is available from appearance potentials. The appearance potential for the formation of the neopentyl ion from 2,2-dimethylbutane corresponding to the process



$$H_3C\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{—}C_2H_5 + e \longrightarrow H_3C\text{—}\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}\text{—}\overset{+}{C}H_2 + CH_3 + 2e$$

would be about 30 kcal./mole higher than that for the formation of the t-pentyl ion as given above. If a break in the ionization efficiency curve does occur at this energy, it is too small to be detected with the normal distribution of electron energies as used in this work.

This value for $\Delta H_f(\text{neopentyl}^+)$ is of interest in connection with the hydride ion transfer reaction reported by Field and Lampe[13]

$$C_3H_5^+ + \text{neo-}C_5H_{12} \longrightarrow C_5H_{11}^+ + C_3H_6$$

Using $\Delta H_f(C_3H_5^+) = 220$ kcal./mole[7,13] and assuming a neopentyl ion to be formed, this reaction would be 21 kcal./mole endothermic. The formation of a neopentyl ion can therefore be ruled out. If the C_5H_{11} ion has isomerized to t-pentyl$^+$ ($\Delta H_f = 165$ kcal./mole), the reaction becomes exothermic by 10 kcal./mole. On this basis the present data support Field and Lampe's proposal that the $C_5H_{11}^+$ ion formed in this reaction has isomerized to a t-pentyl ion.

2-Pentyl and 3-Pentyl.—Although the dissociation energy for a secondary C–H bond is not established beyond dispute, there is considerable evidence for a value of 93–94 kcal./mole.[9,14] Assuming $D(s\text{-pentyl-H}) = 93$ kcal./mole, the heat of formation of 2-pentyl and 3-pentyl radicals becomes 5.9 kcal./mole. The ionization potentials

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(11) M. B. Koffel and R. A. Lad, *J. Chem. Phys.*, **16**, 420 (1948).

(12) E. I. Hormats and E. R. Van Artsdalen, *ibid.*, **19**, 778 (1951).

(13) F. H. Field and F. W. Lampe, *J. Am. Chem. Soc.*, **80**, 5587 (1958).

(14) G. C. Fettis and A. F. Trotman-Dickenson, *ibid.*, **81**, 5260 (1959).

in Table III then give about 184–187 kcal./mole for the heats of formation of 2-pentyl and 3-pentyl ions. This is not at all in agreement with a heat of formation derived from the appearance potential of what might be expected to be a *s*-pentyl fragment ion. For instance, we find that $A(C_5H_{11}^+)$ from 2-methylpentane is 10.6_1 v., using the curve matching procedure.[15] This gives $\Delta H_f(C_5H_{11}^+) \leq$ 172 kcal./mole, that is, about 14 kcal./mole lower than the value derived above for 2-pentyl ion. One possibility is that this fragment ion is a 2-pentyl ion in a configuration which contains some 14 kcal./mole less energy than that formed by direct ionization of a 2-pentyl radical. On this basis the vertical ionization potential would have to be at least 0.6 v. higher than the adiabatic value. It is also possible that in this dissociative ionization the 2-pentyl ion is isomerized to a *t*-pentyl ion, for which $\Delta H_f = 165$ kcal./mole, with an excess energy of about 7 kcal./mole. In view of the formation of *s*-pentyl ions from normal alkanes,[6] such a rearrangement is not unreasonable.

From the appearance potentials of $C_5H_{11}^+$ ions from *n*-heptane and *n*-octane, Stevenson[6] obtained the relation $D(s\text{-}C_5H_{11}\text{–}H) + I(s\text{-}C_5H_{11}) = 10.88$ v. Assuming $D(s\text{-}C_5H_{11}\text{–}H) = 93$ kcal/mole, as above, this relation leads to an ionization potential of 6.85 v. This is about one volt lower than the vertical ionization potential found in this work, and is in fact, slightly lower than that found for *t*-C_5H_{11} radical. A re-measurement of the appearance potential for $C_5H_{11}^+$ from *n*-heptane in our instrument, however, gave 10.8 v.[16] The difference between this and the 10.1 v. reported by Stevenson appears to be too large to be accounted for on the basis of different methods for evaluating the ionization threshold. No explanation for the difference can be offered at present. Although both of these values are consistent with a rearrangement of the pentyl ion from the original primary structure, the uncertainty is so great that no decision can be made at present as to whether the rearranged ion is a secondary or a tertiary ion.

[15] Using the vanishing-current method, the appearance potential is 10.6_5 v. Koffel and Lad,[11] using the linear extrapolation method, also found 10.6 v. for this appearance potential. In this case the ionization efficiency curves for mass 71$^+$ and the xenon standard were found to be very nearly parallel when normalized to the peak height at 50 v. and plotted on a logarithmic scale. For curves of this type appearance potentials obtained by the linear extrapolation method can be quite close to those obtained by the other methods.

[16] When normalized to the 50 v. peak height, the curves for $C_5H_{11}^+$ and xenon were parallel within 0.1 v. between 1% and 0.1% of the 50 v. peak height. Evaluation of the curves by the vanishing current method gave the same value, 10.8 v.

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The Reaction of Carbon Suboxide with Oxygen Atoms

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The reaction of carbon suboxide C_3O_2 with oxygen atoms in a fast flowing gas system was investigated. Oxygen atoms were produced in a Wood discharge tube. Carbon suboxide was introduced into the atom gas stream through a small nozzle. In the reaction zone, a spherical flame occurred. The spectrum of this flame featured the "triplet" bands of carbon monoxide due to the transition CO ($d^3\,\Pi$) → CO ($a^3\,\Pi$). In addition, some of the Swan bands and the persistent CH bands were observed, the latter being attributed to minor impurities. The gas mixture evolving from the reaction was analyzed for CO and CO_2 by means of gas chromatography. The molar ratio CO/CO_2 was found to be about 14:1. No carbon deposit was formed at the walls. A reaction scheme is discussed which is consistent with the observed results. The experiments were carried out to confirm some features of the mechanism suggested in 1955 by Harteck and Dondes for the radiolysis of carbon monoxide and carbon dioxide.

Introduction

The mechanisms controlling the radiolysis of carbon monoxide, the radiolytic oxidation of carbon monoxide in the presence of oxygen and the surprising stability of carbon dioxide against ionizing radiation[2] can be understood if the typical features of these processes are assumed to depend on the intermediate presence of carbon suboxide species like C_2O or C_3O_2.

Based on this assumption, Harteck and Dondes[3] have proposed the following reaction scheme in which carbon atoms and oxygen atoms are supplied by direct radiative dissociation or by ion reactions in the systems mentioned.

$$C + CO + M \longrightarrow C_2O + M \tag{1}$$

$$C_2O + CO + M \longrightarrow C_3O_2 + M \tag{2}$$

$$xC_3O_2 \longrightarrow (C_3O_2)_x \text{ (polymerization)} \tag{3}$$

$$C_2O + O \longrightarrow CO_2 + C \tag{4a}$$

$$C_2O + O \longrightarrow 2CO \tag{4b}$$

$$C_3O_2 + O \longrightarrow 3CO \tag{5a}$$

$$C_3O_2 + O \longrightarrow C_2O + CO_2 \tag{5b}$$

The reactions in irradiated pure CO will essentially follow equations 1, 2, 3 and 4a yielding suboxide polymers and CO_2. The high G-value of 18–24[2] for the oxidation of CO in presence of oxygen and also the stability of CO_2 to ionizing radiation may be explained by means of chain reactions which are constituted by equations 1 and 4a, or 2 and 5b. This explanation implies, however, that one of these chain reactions is considerably faster than all competing and terminating reactions such as (4b) and including the three-body recombinations as well as the direct combi-

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[2] For comprehensive reference see: S. C. Lind, "Radiation Chemistry of Gases," Reinhold Publishing Co., New York, N. Y., 1961, pp. 112–123, 143–145.

[3] P. Harteck and S. Dondes, *J. Chem. Phys.*, **23**, 902 (1955); *ibid.*, **26**, 1727 (1957); *Z. Elektrochem.*, **64**, 983 (1960).