Reports

Positive-Ion Chemistry: High Yields of Heavy Hydrocarbons from Solid Methane by Ionizing Radiation

Abstract. *At 77°K solid methane is polymerized rapidly and efficiently to heavy hydrocarbons by cobalt-60 gamma rays. The product is a viscous oil consisting mainly of saturated and highly branched hydrocarbons containing an average of about 20 carbon atoms per molecule. This would seem to be evidence for positive-ion chemical reactions in the solid state analogous to those previously reported to occur in the gaseous state at pressures above 0.01 mm-Hg. It would thus appear that the solar ionizing ultraviolet radiation (about 1 erg cm^{-2} sec^{-1} at the earth) must polymerize methane at an appreciable rate under many likely conditions.*

Polymer formation in irradiated gaseous methane has been observed by several investigators, and recent studies (*1, 2*) including the use of nitric oxide as free-radical scavenger virtually prove that the polymer is formed by way of a chain of ion-molecule reactions. Such reactions often occur on every collision of the ion with a methane molecule as is directly observed in the source chamber of the mass spectrometer operated at methane pressures of a few tenths of a millimeter of mercury (*3*).

We wish to report our preliminary observations of a viscous polymeric oil which is produced in solid methane at 77°K by the action of Co^{60} gamma rays. We believe that this polymer represents an important example of a radiation-induced process in a condensed phase which cannot be attributed to reactions of neutral free radicals. By analogy to the gas-phase polymer (which is very similar in its properties to our product), it is strongly suggested that the solid-phase polymerization procedes by way of an ion-molecule chain reaction.

Our present evidence indicates that the polymer is formed in direct proportion to the radiation dose, with a conversion of about one methane molecule per 100 ev of absorbed energy (*6*). The only other significant hydrocarbon product is ethane [$G(C_2H_6 \simeq 2]$, which together with the polymer accounts for the observed hydrogen yield of $G(H_2) \simeq 3$. Solid methane was irradiated in 20-gram amounts at 77°K in a Pyrex cell equipped with a break-seal and with an unfilled volume of about 2 ml. The methane was purified to contain no more than 50 parts of ethane per million, and was subjected to a dose of 34 Mrad ($34 \cdot 10^8$ erg/g). This dose converts 0.06 percent of the methane to 12 mg of a viscous oil which is recovered by removing the methane at 77°K at reduced pressure. The radiation-produced ethane (~ 60 mg) is also recovered in the process. Experiments with smaller samples which were analyzed by vapor-phase chromatography show that the yields of hydrogen and ethane are constant within experimental error in the dose range of 1 to 30 Mrad; even at the lowest doses, there is considerable hydrogen in excess of that due to ethane formation. Therefore, the polymer must be produced at such low doses that the conversion of methane is less than 100 ppm.

Four of the 20-gram samples were irradiated to 0, 28, 34, and 75 Mrad, at a rate of about 0.7 Mrad/hr, except for one which received a total of 34 Mrad at the rate of 0.25 Mrad/hr. The weight of recovered ethane and polymer was directly proportional to the dose, within our error of about 20 percent, to give the indicated yields. Nuclear magnetic resonance analysis of the product obtained from irradiation with 75 Mrad and later dissolved in dilute carbon tetrachloride solution showed a broad methyl peak and a broad methylene peak whose areas indicate that the sample contained somewhat more than twice as many methyl as methylene hydrogens. The absence of a resonance due to vinyl hydrogen places an upper limit of about 5 percent on the vinyl hydrogens and consequently on unsaturation. This high degree of branching and saturation is similar to that observed in the gas-phase polymer (*1*).

Determinations of average molecular weight by vapor-pressure osmometry (which tends to emphasize the low molecular weights) of the products of irradiation at 28 and 34 Mrad in chloroform solution gave identical values corresponding to C_{18} components, which would indicate that the postulated chain mechanism is terminated in a manner not strongly influenced by the dose rate. It is interesting that vapor-phase chromatographic analysis of the recovered ethane and other products volatile at 0°C showed over 30 distinct peaks, representing compounds of molecular weight up to that of C_7H_{16}. The 13 largest peaks match very well with the retention times of the five straight-chain hydrocarbons (propane through heptane) plus certain single- and double-branched saturated hydrocarbons. Quantitatively, these products are very minor; few of them represent G values greater than about 10^{-4}; many are in the 10^{-6} range. None of the larger peaks can be due to impurities in the original methane, as indicated by analysis of the unirradiated sample, but they are small enough to have possibly been produced in the 1 cm of mercury vapor pressure of methane in the 2-ml gas phase above the solid. However, the oil could not have been so formed since its yield would in that case have to be $G(\text{-}CH_4) > 10^5$, about 10^5 times larger than reported in the gas at higher temperature and pressure (*1*).

There are possible broad implications for radiation chemistry in the solid and liquid phase. Our present belief is that the most likely reactions are due to the carbonium ions CH_3^+, $C_2H_5^+$, . . . $C_nH_{2n+1}^+$ which, in the case of methane, are formed by CH_3^+ and its progeny by reaction with methane. The branched nature of the methane polymer would thereby be explained by the greater stability of secondary and tertiary carbonium ions compared to primary ions (*4*).

At the present intensity (1 erg cm^{-2} sec^{-1}), the solar ionizing ultraviolet would produce about 100 rad/sec in a film of solid 1 micron thick—the approximate range of the radiation. Thus we see that except possibly for the most dilute gases (less than 0.01 mm-Hg pressure) the very rapid polymerization reaction described here must occur on the surface of solid, liquid, or even gaseous methane, the yield being about 0.01 percent per day in the top layer. Any other source of ionizing radiation would add to this. We suspect that this phenomenon is general and applies to other gases as well. It has wide implications for the origin of the large molecules necessary for the origin and support of life as well as for an understanding of the composition of meteoritic and planetary matter.

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References and Notes

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4. Similar reasoning is used to understand Markovnikoff's rule for the direction of addition of reagents such as HBr to unsymmetrical double bonds. See for example, D. J. Cram and G. S. Hammond, *Organic Chemistry* (McGraw-Hill, New York, 1959), p. 336.
5. This is paper No. IV of a series "Positive Ion Chemistry." Supported in part by the U.S. Air Force Office of Scientific Research grant No. AF-AFOSR-245-64.

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Affinity and Phosphorylation Constants for the Inhibition of Esterases by Organophosphates

Abstract. *Equations based on the assumption of a reversible first step in the reaction between organophosphate inhibitors and esterases are proposed for the bimolecular rate constant which now includes an affinity constant and a phosphorylation constant. The treatment applies when the inhibition reaction follows first-order kinetics.*

The bimolecular rate constant k_i is generally considered to be the most reliable criterion by which to measure the inhibitory power of an organophosphate for an esterase. The equation for evaluating k_i is based on the assumption that the organophosphate I and the esterase E react directly to form the irreversibly phosphorylated active center (EI_q) (*1*). This clearly implies that k_i is simply a phosphorylation constant. Perhaps because of this implication, studies which have attempted to relate the structure of inhibitors to their inhibitory power have tended to interpret structure largely in terms of phosphorylation potential. Correlation between phosphorylation potential, as expressed for example by the Hammett constant (*2*), and inhibitory power has in general been only moderately good (*3, 4*), and at times there has been no correlation (*5*).

Inhibitory power is also expressed by (I_{50}), which is an empirical value, but which may be considered as a "loosely" defined function of k_i (*4*).

In contrast to the assumptions on which k_i is based, it is widely accepted that the reaction between the organophosphate and the esterase probably involves a reversible step which precedes phosphorylation and results in formation of an enzyme-inhibitor complex $(EI)_r$ (*6*).

The inhibition reaction is then,

$$\underset{e}{E} + \underset{i}{I} \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \underset{r}{(EI)_r} \xrightarrow{k_p} \underset{q}{(EI)_q} \qquad (1)$$

where e and i are the initial concentrations of E and I, and r and q are the concentrations of $(EI)_r$ and $(EI)_q$, respectively. The individual rate constants are k_1, k_2, and k_p.

The reversible step will depend on the affinity of the inhibiting compound for the active site and is governed by the affinity constant K_a where $K_a = k_2/k_1$. Irreversible phosphorylation is governed by the phosphorylation constant k_p.

According to this interpretation, inhibitory power will depend on the affinity of the organophosphate for the active site of the esterase as well as on the rate of phosphorylation. But present procedures (*1, 7, 8*) ignore the possibility of a reversible step and the consequent affinity constant. What then is the relationship between k_i as it has been determined and K_a and k_p? Furthermore, it seems legitimate to consider whether the experimental procedures which have been used for determining k_i are adequate within the context of a reversible step.

One possible solution is given in the following treatment. The rate at which $(EI)_r$ is formed will be proportional to the concentration of free enzyme $(e - r - q)$ and to the inhibitor concentration. For real values of i and assuming $k_2 > 0$, it is evident that only a fraction of the enzyme remaining uninhibited at any instant during the reaction, that is $(e - q)$, will be in the form of $(EI)_r$. If i is substantially greater than e, it will remain essentially constant over the course of the reaction.

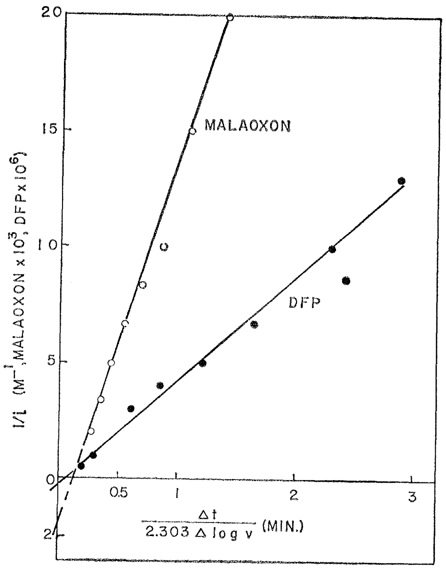

Fig. 1. Plot of the reciprocal of the inhibition rate ($\Delta t/2.303\ \Delta \log v$) against the reciprocal of the inhibitor concentration ($1/i$) according to Eq. 10 for the reactions of DFP and malaoxon with human serum cholinesterase at 37°C, *p*H 7.6. The unit of the ($1/i$) scale is $10^6\ M^{-1}$ for DFP and $10^3\ M^{-1}$ for malaoxon. The slopes gives k_i, the "bimolecular reaction constant," and the intercepts of the extrapolated lines on the ordinate and abscissa give ($-1/K_a$) and ($1/k_p$). The K_a and k_p values for malaoxon were $7.7 \times 10^{-4}\ M$ and 11 min^{-1}, respectively. Corresponding values for DFP could not be reliably determined, although estimates were made.

The reaction between E and I follows first-order kinetics over significant ranges of inhibitor and esterase concentrations when i is constant (*7, 9*). The fraction of the esterase in the form of reversible enzyme-inhibitor complex must then bear a constant relationship to the total available esterase. That is, the ratio $[r/(e - q)]$ must be constant. The reversible reaction will then approximate a steady state at any instant during the reaction from which,

$$k_1 (e - r - q) i = k_2 r, \qquad (2)$$

and

$$r = \frac{(e - q) i}{i + K_a} \qquad (3)$$

The rate of irreversible inhibition is

$$\mathrm{d}q/\mathrm{d}t = k_p\, r \qquad (4)$$

Substituting Eq. 3 into Eq. 4 gives

$$\mathrm{d}q/\mathrm{d}t = \frac{i}{(i + K_a)}\, k_p\, (e - q) \qquad (5)$$

According to Eq. 5 the reaction is first-order with respect to e when i is constant.

Integrating Eq. 5 between the limits