The procedure above was applied to 1-bromonaphthalene which released 88% of the theoretical amount of bromide ion and gave 3.5 g. (84%) of crude 1-naphthol. The phenylurethan derivative melted at 173–175° (rec. m.p. 176°), and the melting point of a mixture with an authentic sample was not depressed.

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[CONTRIBUTION FROM THE RADIATION LABORATORY, CONTINENTAL OIL COMPANY]

The Role of Free Radical Processes in the γ-Radiolysis of Methane, Ethane and Propane

BY KANG YANG AND PETER J. MANNO

RECEIVED DECEMBER 27, 1958

Nitric oxide inhibits the formation of hydrogen and saturated hydrocarbons in the γ-radiolysis of methane, ethane and propane. From these inhibition data, the $F_M(X)$-value (per cent. free radical contribution to the production of a species X in the γ-radiolysis of a compound M) has been determined. The $F_M(X)$-values for the chain degradation products are smaller than the $F_M(X)$-values for the products having carbon numbers larger than M. For example, $F_{C_3H_8}(X)$-values for various products are: H_2, 58; CH_4, 36; C_2H_6, 32; n-C_4H_{10}, 75; i-C_4H_{10}, 91; i-C_5H_{10}, 100. At present, nitric oxide appears to be most satisfactory for the estimation of radical energy yields, as well as contributions of free radical reactions to radiolysis of gaseous hydrocarbons.

Introduction

Interpretation of products yield in radiolysis of hydrocarbons is complicated by a number of potential processes which may contribute to the over-all mechanism. The problem may be partially simplified by the use of "so-called" radical scavengers[1–4] (as well as isotopic exchange method)[1,5–7] to determine the relative contribution of thermalized free radical processes, as compared to other possible processes. While the results of such observations are not unambiguous, as will be noted later, they may serve well as starting points for the complete elucidation of the radiolysis mechanism.

In the following sections, it is convenient to present our data in terms of a derived parameter $F_M(X)$, which we define as the % decrease in the yield of product X resulting from the addition of a radical scavenger during the radiolysis of compound M. The scavenger used in our work was nitric oxide. If it is assumed that the scavenged portion represents the free radical contribution and the remainder the contribution of non-free radical processes, then $F_M(X)$ is equivalent to the % free radical contribution to the formation of species X. It probably is safe to conclude that few, if any, free radical processes occur in the presence of a sufficient concentration of NO. However, it is possible that a charge transfer reaction of the type

$$RH^+ + NO \longrightarrow NO^+ + RH \qquad (1)$$

may occur, complicating interpretation of the inhibition data. In any case, this reaction probably could not compete with the ion–molecule reaction of the type[8,9]

$$RH^+ + M \longrightarrow \text{Products} \qquad (2)$$

under the condition of $[NO]/[M] \simeq 0.06$, where maximum inhibition has been reached already. In fact, comparison of the values obtained from our data with those obtained by other methods suggests that the error attributable to the reactions of type 1 is not great and the $F_M(X)$ is a reasonable approximation to the % free radical contribution.

Experimental

Phillips research grade methane was purified by bulb-to-bulb distillation in a high vacuum line. Phillips research grade ethane and propane and Matheson nitric oxide (min. 99%) were degassed by a freeze-pump technique and subjected to bulb-to-bulb distillation on a high vacuum line. The only detectable impurities in the resulting gases were 0.1% ethane in methane (GLPC) and 0.3% nitrous oxide in nitric oxide (mass spectrometric analysis). The irradiation vessel was made of Pyrex glass and equipped with breakoff seal and capillary constrictions at opposite ends. This vessel was charged with purified hydrocarbons (at 60 cm.) and varying amounts of nitric oxide (maximum 12%). Four spent fuel elements (150 days cool), from the Materials Testing Reactor, Arco, Idaho, shielded by 5.5 meters of water were used as an irradiation source. All experimental data were obtained at 22.5 ± 1° (the ambient temperature of the water). Gamma field intensity was determined by an air-gap ionization chamber calibrated with a cerous–ceric sulfate chemical dosimeter.[10] Ionization chamber readings before and after each run were averaged. To calculate the amounts of energy absorbed by each sample, it was assumed that the absorption coefficients were proportional to the electron density of the material. The energy input rate was approximately 2×10^{19} e.v. per g. per hour. After irradiation, the gaseous products were analyzed by gas chromatography. The products did not exceed 1% of the reactant. The analytical conditions were

Gas analyzed	Anal. conditions
Hydrogen and methane	Silica gel column, 2 m., 25°, nitrogen carrier, 25 cc./min.
Ethane and ethylene	High-activity charcoal column, 2 m., 149°, helium carrier, 84 cc./min.
Propane, propylene and acetylene	Silica gel column, 2 m., 87°, helium carrier, 30 cc./min.
Butanes, butenes and pentanes	Hexamethylphosphoramide, 4.6 m., 25°, helium carrier, 75 cc./min.

Results

Methane Radiolysis.—The effect of nitric oxide on the radiolysis of methane is summarized in Table I and depicted in Fig. 1. The various prod-

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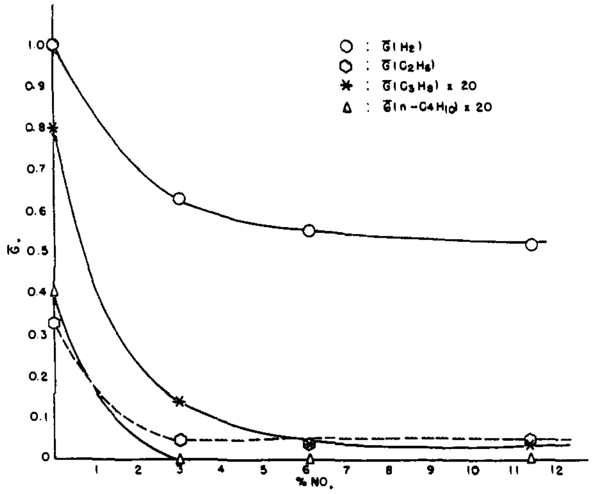

Fig. 1.—Relative energy yields of hydrogen, ethane, propane and *n*-butane in the γ-radiolysis of methane as a function of nitric oxide concentration.

ucts detected are listed in the first row of the table. The relative energy yields of these products are reported using the quantity $\bar{G}$(product) defined as

$$\bar{G}(\text{product}) = G(\text{product})/G(H_2)_0$$

The number of hydrogen molecules formed per 100 e.v. of energy absorbed in the uninhibited radiolysis of methane, $G(H_2)_0$, was 6.4. $\bar{G}$-values for various products at zero concentration of nitric oxide are summarized in the second row of Table I. Upon the addition of nitric oxide, $\bar{G}$-values for the saturated products decreased sharply and reached a constant value at nitric oxide concentrations larger than 6% (Fig. 1). These limiting $\bar{G}$-values are listed in the third row of Table I. The calculated % free radical contributions are given in the fourth row. Our result, $F_{CH_4}(H_2) = 44$, agrees well with the published value of 50 estimated by isotopic exchange and radical scavenger method.[6] In sharp contrast to the inhibition of the formation of saturated hydrocarbons, the $\bar{G}$(ethylene) increased with increasing nitric oxide concentration and reached a limiting value when more than 6% nitric oxide was added. Probable reactions which may be responsible are an inhibition of the reaction, $H + CH_2{=}CH_2 \rightarrow CH_3CH_2$, by nitric oxide or a disproportionation type reaction, $NO + CH_3CH_2 \rightarrow HNO + CH_2{=}CH_2$.

Ethane Radiolysis.—In the γ-radiolysis of ethane, the products detected and their $\bar{G}$-values are summarized in Table II. The $G(H_2)_0$ in ethane radiolysis was 6.8 molecules per 100 e.v.[11] The effect of nitric oxide on the $\bar{G}$-value for the saturated products is shown in Fig. 2. (Our result, $F_{C_2H_6}(H_2) = 41$, is in reasonable agreement with the results of Dorfman of ≤ 50 (by isotopic exchange method)[5,12] and 34 (by ethylene scavenger data).)[1] Our result, $F_{C_2H_6}(CH_4) = 44$, also agrees well with his result of ≤ 50 determined by isotopic exchange method.[1] The estimated free radical contribution for propane, butanes and pentanes was larger than that for methane, suggesting that free radical reactions participated more heavily in chain lengthening processes in comparison to chain degradation processes.

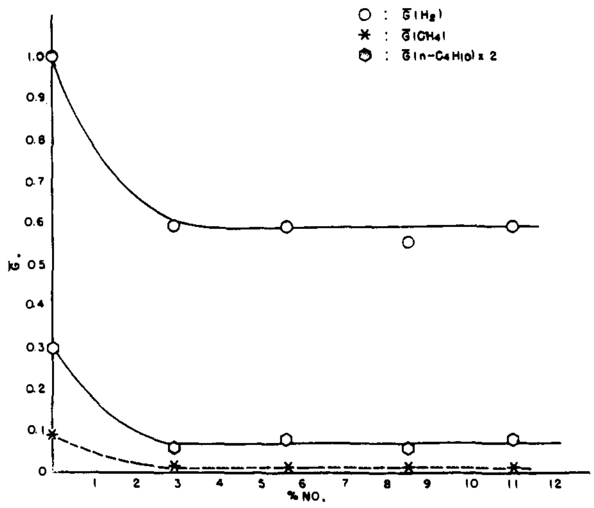

Fig. 2.—Relative energy yields of hydrogen, methane and *n*-butane in the γ-radiolysis of ethane as a function of nitric oxide concentration.

Propane Radiolysis.—The products detected and their relative energy yields obtained in the γ-radiolysis of propane are summarized in Table III. The $\bar{G}(H_2)_0$ in propane radiolysis was 5.9 molecules per 100 e.v.[12] Nitric oxide strongly inhibited the formation of saturated products (Fig. 3). $F_{C_6H_8}$-(X)-values for butanes and pentanes were larger than those for methane and ethane, also suggesting a larger contribution of free radical reactions in chain-lengthening processes than in chain degradation processes.

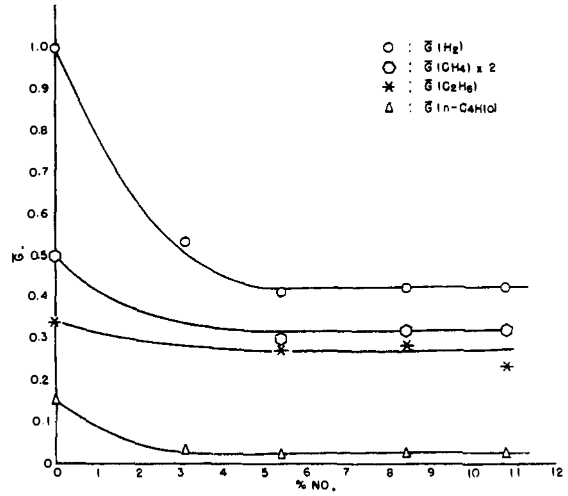

Fig. 3.—Relative energy yields of hydrogen, methane, ethane and *n*-butane in the γ-radiolysis of propane as a function of nitric oxide concentration.

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[11] Our results, $G(H_2)_0 = 6.8$ in ethane radiolysis and $G(H_2)_0 = 5.9$ in propane radiolysis, are slightly higher than the values 5.0 and 4.26, in α-particle induced decomposition of ethane and propane, respectively (*cf.*, B. M. Tolbert and R. M. Lemmon, *Radiation Research*, **3**, 52 (1955)). One of the sources of discrepancy may be the difference in dosimetric standard and methods of calculating energy absorbed by the samples.

[12] Referee informed us that more recent value is ≤ 40, which agrees more closely with our result.

TABLE I

FREE RADICAL CONTRIBUTIONS IN THE γ-RADIOLYSIS OF METHANE

Products	H_2	C_2H_6	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	i-C_5H_{10}	C_2H_4	C_3H_6
$\bar{G}^a$ (NO absent)	1.00	0.33	0.04	0.02	0.01	0.007	0.02	0.000
$\bar{G}^a$ (NO present)	0.56	0.05	0.002	0.00	0.00	0.000	0.10	0.005
F-Value (% radical cont.)	44	85	85	100	100	100	..	...

[a] $\bar{G}$(Product) = G(Product)/$G(H_2)_0$, $G(H_2)_0$ was 6.4 (molecules per 100 e.v.).

TABLE II

FREE RADICAL CONTRIBUTIONS IN THE γ-RADIOLYSIS OF ETHANE

Products	H_2	CH_4	C_3H_8	n-C_4H_{10}	i-C_4H_{10}	i-C_5H_{10}	C_2H_4	C_3H_6	C_4H_8	C_2H_2
$\bar{G}^a$ (NO absent)	1.00	0.09	0.08	0.15	0.005	0.08	0.008	0.000	0.000	0.00
$\bar{G}^a$ (NO present)	0.59	0.05	0.02	0.04	0.000	0.00	0.20	0.004	0.002	0.04
F-Value (% radical cont.)	41	44	75	73	100	100	...	...	...	..

[a] $\bar{G}$(Product) = G(Product)/$G(H_2)_0$, $G(H_2)_0$ was 6.8 (molecules per 100 e.v.).

TABLE III

FREE RADICAL CONTRIBUTIONS IN THE γ-RADIOLYSIS OF PROPANE

Products	H_2	CH_4	C_2H_6	n-C_4H_{10}	i-C_4H_{10}	i-C_5H_{10}	C_2H_4	C_3H_6	C_4H_8	C_2H_2
$\bar{G}^a$ (NO absent)	1.00	0.25	0.34	0.04	0.11	0.07	0.04	0.04	0.002	0.03
$\bar{G}^a$ (NO present)	0.42	0.16	0.23	0.01	0.01	0.00	0.12	0.22	0.003	0.06
F-Value (% radical cont.)	58	36	32	75	91	100	..	..	...	..

[a] $\bar{G}$(Product) = G(Product)/$G(H_2)_0$, $G(H_2)_0$ was 5.9 (molecules per 100 e.v.).

Discussion

The F_M(X)-Values and Mass Spectral Data.—Burr attempted a correlation of F_M(X)-values to the mass spectral patterns of M but failed to obtain quantitative agreement.[4] One of the shortcomings in his method is only a single decomposition of an ion is considered, even though many decomposition modes are possible and are observed in mass spectrometry. In some simple cases, this shortcoming could be minimized. For example, if we consider only those reactions which yield ions having relative peak sizes of more than 5, then the cracking pattern for methane could be represented by the reactions[13,14]

		m/e	Relative peak sizes
(3)	$CH_4 \rightsquigarrow CH_4^+ + e$	16	100
(4)	$CH_4 \rightsquigarrow CH_3^+ + H + e$	15	85.9
(5)	$CH_4 \rightsquigarrow CH_2^+ + H_2 + e$	14	16.1 (*cf.* note 15)
(6)	$CH_4 \rightsquigarrow CH^+ + 3H + e$	13	8.09

Suppose that all hydrogen atoms undergo the reaction

$$H + CH_4 \longrightarrow CH_3 + H_2 \qquad (7)$$

then the calculated $F_{CH_4}(H_2)$-value is 87. If the reaction producing CH^+ ions was

$$CH_4 \rightsquigarrow CH^+ + H_2 + H + e \qquad (8)$$

then $F_{CH_4}(H_2)$ becomes 80. In both cases, these values are far from the experimental value of 44 (*cf.* Table I). This discrepancy may come from reactions that occur in the radiolysis of M, which are negligible or not detected under the conditions used in obtaining the mass spectral patterns of M. Two possible contributing reactions of importance are

(a) Ion–molecule reactions: $RH^+ + M \longrightarrow$ Products

(b) Decomposition of excited M to neutral fragments

$$\begin{tikzcd} & M^* \arrow[r] & R_1 + R_2, \text{ etc.} \\ M \arrow[ur, squiggly] \arrow[dr, squiggly] & & \\ & M^+ + e \arrow[uu] & \end{tikzcd}$$

If we recalculate $F_{CH_4}(H_2)$ value to include an important ion–molecule reaction[8]

$$CH_3^+ + CH_4 \longrightarrow C_2H_5^+ + H_2 \qquad (9)$$

then $F_{CH_4}(H_2)$ reduces to 52 in good agreement with the experimental value of 44. However, this agreement may be fortuitous because various other possible ion–molecule reactions, such as[9,16]

$$C_2H_5^+ + CH_4 \longrightarrow C_3H_7^+ + H_2 \qquad (10)$$

and decomposition of excited molecules have not been included.

Radical Reactions.—A quantitative description of reactions not inhibited by nitric oxide is not possible with the presently available knowledge; but those occurring by radical processes could be discussed using known reactions.[17] For example, the formation of hydrogen in ethane radiolysis produced by radical processes is probably due to the reactions

$$C_2H_6 \rightsquigarrow H + \text{Products} \qquad (11)$$

$$H + C_2H_6 \xrightarrow{k_{12}} H_2 + C_2H_5\cdot \qquad (12)$$

Energy yield of hydrogen produced by these processes is 2.8 molecules per 100 e.v. If we neglect radical recombinations, such as

$$H + R \longrightarrow RH \qquad (13)$$

$$H + M + R \longrightarrow RH + M \qquad (14)$$

then the steady-state concentration of hydrogen atom [H] becomes

$$[H] \simeq 6 \times 10^{-14} \text{ mole per liter}$$

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(13) "Catalog of Mass Spectral Data," A.P.I. Project 44, Carnegie Institute of Technology, Pittsburgh, Series No. 1.

(14) F. H. Field and J. L. Franklin, "Electron Impact Phenomena," Academic Press, Inc., New York, N. Y., 1957, pp. 247-261.

(15) The suggestion that the hydrogen detached molecularly from ethane was from the reaction

$$C_2H_6^+ \longrightarrow C_2H_4^+ + H_2$$

was first made by Dorfman.[5]

(16) F. H. Field, J. L. Franklin and F. W. Lampe, THIS JOURNAL, **79**, 2419 (1957).

(17) E. W. R. Steacie, "Atomic and Free Radical Reactions," Reinhold Publ. Corp., New York, N. Y., 1954.

at an energy input rate of 1.6×10^{15} e.v. per g. sec. ($\approx 10^5$ rep. per hr.), [M] = 1 atm., and at 25°. For this estimation

$$k_{12} = 3.4 \times 10^{12} \exp(-6800/RT) \text{ cm.}^3 \text{ mole}^{-1} \text{ sec.}^{-1}$$

was used.[18] Concentrations of other radicals are probably of the same order of magnitude or less. Hence, at the experimental conditions employed in our work, the rate of reaction 12 is approximately 10^4 and 10^7 times faster than the rate of reactions 13 and 14, respectively, even if a steric factor of 1 is assumed for the latter processes.[19] Thus, the aforementioned approximation that all radicals undergo hydrogen abstraction reactions seems reasonable. Using this approximation and the nitric oxide inhibition data, G-values for various free radicals are calculated

M \ Radical	H	CH_3	C_2H_5
CH_4	2.8	[a]	..
C_2H_6	2.8	0.3	[a]
C_3H_8	3.4	0.5	0.6

[a] Not able to estimate with the present method.

Due to the probable uncertainty arising from the contribution of radical recombination in chain lengthening processes, G-values for the radicals having a larger carbon number than the reactant are not estimated.

Meisels, Hamill and Williams[6] reported an ion pair yield of 1 for H in the radiolysis of argon + methane system, using both an isotopic exchange and a radical scavenger method (propylene). Since energy required[20] to produce an ion pair in methane by α-particle irradiation is 31 e.v., their estimation corresponds to a G(H) = 2.8, in agreement with our result of 3.2.

Iodine probably is better than nitric oxide to identify individual free radicals[21]; but its use to estimate radical G-values is not advisable. Iodine does not inhibit the formation of hydrogen in methane radiolysis.[6] Since 41% of the hydrogen formed arises from radical processes, the above observation suggests that iodine cannot inhibit the type of reaction 7. Hence, the iodine method gives ambiguous energy yields for hydrogen atom and for those radicals produced by the interaction of hydrogen atom with the reactants. Hydrogen iodide accelerates the formation of hydrogen in methane radiolysis,[6] and its use involves similar uncertainties. Ethylene and propylene produce hydrocarbons such as methane, ethane and propane by reacting with hydrogen atoms and hydrocarbon free radicals produced by γ-irradiation.[22] For this reason, their use is also not advisable. Therefore, it appears that nitric oxide is one of the few radical scavengers which is satisfactory to estimate the energy yield of radicals, as well as the contributions of free radical reactions to the over-all radiolysis of gaseous hydrocarbons.

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[18] M. R. Berlie and D. J. LeRoy, *Disc. Faraday Soc.*, **14**, 50 (1953).

[19] Collision theory is used for this estimation.

[20] W. P. Jesse and J. Sadanokis, *Phys. Rev.*, **97**, 1668 (1955).

[21] L. H. Gevantman and R. R. Williams, Jr., *J. Phys. Chem.*, **56** 569 (1952).

[22] This result will be published later.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Photolysis of Acetone in Some Fluorinated Solvents[1]

BY D. B. PETERSON AND GILBERT J. MAINS

RECEIVED DECEMBER 18, 1958

Acetone, acetone-d_6 and a 1:1 mixture of acetone and acetone-d_6 have been photolyzed in liquid perfluorodimethylcyclobutane and in a liquid fluorinated cyclic ether. The distribution of isotopically substituted methanes and ethanes in the gaseous products is in agreement with a free radical mechanism. The variation of the ratio of the rate of methane production to the square root of the ethane production rate with acetone concentration is linear as suggested by the free radical mechanism. The ratio of the specific rate constant for hydrogen abstraction to the square root of the specific rate constant for ethane production is in agreement with vapor phase studies when diffusion is taken into account. Because the difference in the quantum yields of gaseous products in the fluorinated solvents cannot be attributed to "caging" effects, a difference in the yield of methyl radicals from the primary process due to quenching of the excited electronic state of acetone by these solvents is suggested as a possible explanation.

Introduction

Photochemical studies have been made of pure liquid acetone[2-5] and of solutions of acetone in various solvents.[2-6] In the early studies[2,3,6] gaseous products were not detected. Subsequent investigations[4,5] revealed that carbon monoxide, methane and ethane are produced, but at quantum yields considerably lower than are observed in the vapor phase photolysis.

The interpretation of the results of the photolysis of pure liquid acetone is complicated by the rather poor analytical precision inherent to systems with low quantum efficiencies and by the inhomogeneous nature of the light absorption. Previous photo-

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[1] Based on a thesis submitted by D. B. Peterson in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Carnegie Institute of Technology.

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