curvature owing to an appreciable variation in the solubility. The effect of solubility on the curvature of such a plot is discussed elsewhere in sufficient detail.[9]

(9) A. E. Hirschler, THIS JOURNAL, 58, 2472 (1936).

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NOTRE DAME]

A Study of Effect of Impingement-Particle Velocity in Radiolysis of Some Aromatic Hydrocarbons[1,2,3]

BY THOMAS J. SWORSKI[4] AND MILTON BURTON

Total-gas 100 ev. yields (*i.e.*, *G* values) in radiolysis of toluene, ethylbenzene, *i*-propylbenzene and *t*-butylbenzene in the Oak Ridge nuclear reactor are, respectively, 0.18, 0.27, 0.27 and 0.22, all values being slightly higher (10–30%) than yields obtained in electron bombardment radiolysis. At the same time, in every case studied, the ratio $G(H_2)/G(CH_4)$ is increased in reactor exposures over the ratio in electron bombardment by a factor of approximately two, the factor increasing in the order of listing above.

If secondary reactions involving pairs of free radicals can compete with reactions involving single radicals, an essential difference may be expected between effects of slow and fast particle irradiation.[5] The work reported herein was intended to examine such a possibility by radiolysis in a pile of a group of aromatic compounds whose electron-induced radiolysis had already been studied. It was expected that differences obtained would be essentially qualitative because the energy imparted to a sample by radiation in a pile is attributable about half to neutrons and about half to gamma and X-rays. Only product gases volatile at −120° were determined.

Experimental

Preparations of Materials.—Toluene, Baker and Adamson quality, reagent, b.p. range 110–111° was fractionated in a column with 50 theoretical plates. A middle third of constant b.p. was retained; $n^{20}D$ 1.4965, $n^{20}D$ (lit.) 1.4969.

Ethylbenzene, Eastman Kodak White Label, b.p. range 134–136°, was fractionated in a column with 50 theoretical plates. A middle third of constant b.p. was retained; $n^{20}D$ 1.4956, $n^{20}D$ (lit.) 1.4959.

Samples of *i*-propylbenzene and *t*-butylbenzene employed in this work were from batches prepared for previous work on electron irradiation studies.[8]

Techniques for purification of all samples prior to exposure were identical with those previously described.[6]

Exposure Techniques.—The vessels for pile exposure were made entirely of quartz and were of cylindrical shape, internal diameter about 23 mm., internal length about 49 mm., and internal volume about 20 ml. At the end of the cylindrical vessel were attached a quartz break-off seal and a section of quartz tubing with a constricted region to which a graded seal was attached for the duration of the filling operation. Caution had to be exercised in freezing the liquids in the quartz vessels since supercooling resulted in cracking the quartz vessels. To prevent this, the liquids were first slowly frozen by an ethyl bromide mush (−120°); they could then be cooled with liquid nitrogen.

The cells were less than half-filled, with sample volumes ranging from 6 to 9 ml. The samples were exposed for periods of 8 and 16 hours in a central region of the graphite pile at the Oak Ridge National Laboratory. The hole in which the samples were exposed was cooled by a stream of running water maintained at a temperature of 15–20°; the samples were consequently at somewhat higher temperature. (In the electron irradiation studies with which comparison is made, temperature was maintained at about 20–25° by cooling water.)

The four substances herein reported were exposed simultaneously to insure correct relative *G* values. Gas yields were found to be a linear function of exposure.

The following figures for energy dissipation per gram of certain atoms are used in calculation of energy dissipation in their compounds.[7]

Element	Cal. g.$^{-1}$ sec.$^{-1}$
C	0.00046
H	.0075

Analyses.—Analyses of gaseous products for H_2, CH_4 and C_2 fractions were performed in a Saunders–Taylor semimicro gas analysis apparatus[8] essentially as described by Hentz and Burton.[9] The mass spectrometer was used for positive identification of methane and for analysis of the C_2 fraction.

Results and Discussion

The chemical effects of electron irradiation of toluene, ethylbenzene, *i*-propylbenzene and *t*-butylbenzene have been previously reported from these laboratories.[6,9] These same compounds were selected for a study of chemical effects of pile irradiation to determine effect of impingent particle velocity. Table I summarizes the results of this investigation. Table II compares the 100 ev. yields (*G* values) calculable from Table I with results previously obtained on irradiation with 1.5 and 1.8 Mv. electrons.[6,9] The discrepancy between *G* values of hydrogen for pile and electron irradiation is small.

TABLE I

SUMMARY OF PILE IRRADIATION DATA

	% H_2	% CH_4	% C_2 gas	G_t[a]
Toluene	87.6	3.4	9.0	0.18
Ethylbenzene	83.2	8.6	8.2	.27
i-Propylbenzene	77.5	18.5	4.0	.27
t-Butylbenzene	72.1	20.6	8.3	.22

[a] The number of molecules of gas produced volatile at −120° per 100 ev. absorbed.

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(1) Contribution from the Radiation Chemistry Project operated by the University of Notre Dame under Atomic Energy Commission contract AT(11-1)-38.

(2) The nuclear reactor exposures described herein were performed in the graphite reactor of the Oak Ridge National Laboratory.

(3) This paper is an abstract from a thesis submitted by Thomas J. Sworski to the Department of Chemistry of the University of Notre Dame in partial fulfillment of requirements for the degree of Doctor of Philosophy.

(4) Chemistry Division, Oak Ridge National Laboratory, Oak Ridge, Tenn.

(5) *Cf.* M. Burton, *J. Phys. Colloid Chem.*, 51, 611 (1947).

(6) T. J. Sworski, R. R. Hentz and M. Burton, THIS JOURNAL, 73, 1998 (1951).

(7) D. M. Richardson, ORNL-129, The Calorimetric Measurement of Radiation Energy Dissipated by Various Materials in the Oak Ridge Pile.

(8) K. W. Saunders and H. A. Taylor, *J. Chem. Phys.*, 9, 616 (1941).

(9) R. R. Hentz and M. Burton, THIS JOURNAL, 73, 532 (1951).

We do not at this time wish to comment on its reality other than to say that the reliability of G-value determinations for electron irradiation is still under investigation. Not only are relative yields of C_2 gas greater in pile bombardment but, as can be seen from Table III, the H_2/CH_4 ratios are much increased.

TABLE II

G VALUES FOR GAS PRODUCTION IN PILE AND ELECTRON[6,9] IRRADIATION

	$G(H_2)$		$G(CH_4)$		$G(C_2)$	
	Pile	Electron	Pile	Electron	Pile	Electron
Toluene	0.16	0.13	0.006	0.008	0.016	0.001
Ethylbenzene	.22	.18	.023	.030	.022	.004
i-Propylbenzene	.21	.17	.050	.073	.011	.009
t-Butylbenzene	.16	.11	.045	.070	.018	.009

TABLE III

COMPARISON OF H_2/CH_4 RATIOS

Compound	Pile irradiation (p)	Electron irradiation (e)	p/e
Toluene	25.9	16.4	1.58
Ethylbenzene	9.7	5.9	1.64
i-Propylbenzene	4.2	2.3	1.83
t-Butylbenzene	3.5	1.6	2.09

Yields of product were necessarily small to avoid secondary effects; thus mass spectrometric analysis of the C_2 fractions was difficult and more qualitative than quantitative. Table IV shows the C_2 fraction in toluene exposure to consist wholly of ethylene and acetylene, presumably from ring rupture.

TABLE IV

MASS SPECTROMETRIC ANALYSES OF THE C_2 FRACTIONS

	% C_2H_6	% C_2H_4	% C_2H_2
Toluene		58	42
t-Butylbenzene	79		21

Temperature Effect.—Although temperature of the cooling water was known in both pile and electron exposures, the temperatures of the samples were not known—other than that they exceeded the temperature of the coolant. Thus, there might be some suspicion that the results reported represent an undetermined temperature effect. However, in some preliminary experiments on photolysis of toluene and mesitylene, both liquid and vapor, Hentz[10] found that percentage composition of gaseous products was not affected by variation of temperature in the range 50–80°. From experience on similarity of photolysis and radiolysis in these compounds, we may presume that similar results would be found in radiolysis, particularly over the smaller temperature differences such as characterized the pile and electron exposures. The differences exhibited in Tables II and III represent large variations in composition for which some explanation other than the small temperature difference should be offered. Such a conclusion is not too unreasonable if we note that the energy (*i.e.*, the effective temperature) of the radicals which can enter into reaction on a collision soon after their formation is determined by the circumstances of their formation and not by ambient temperature, when the latter is relatively low.

Degree-of-excitation Effect.—In general, C–H rupture requires more energy than C–C rupture.[11] Thus, if conditions of pile exposure are such that the individual excited molecule receives on the average more energy than does a similar molecule exposed to electrons, C–H rupture will be favored and the H_2/CH_4 ratio, as well as total gas yield, will be increased.

Energy loss of charged particles traversing matter has been calculated by Bohr,[12] on a classical mechanical basis, and by Bethe,[13] using quantum mechanics. The results show that more energy is imparted to a single molecule on the average by a slow particle than by a fast one; *i.e.*, for particles of equal energy, by a heavy one (such as a proton) than by a light one (such as an electron). Thus, qualitatively the effect of neutron (heavy particle) contribution to radiolysis in a pile is in the direction that may be expected on the basis of this superficial analysis of the theory involved. Some detailed calculations of the effect of particle velocity on a system of hydrogen atoms have been made by Hentz (private communication). Although the effect is in the right direction, it may be very small and the significance for radiation chemistry is not yet clearly established.

Ionization Density Effect.—Alternatively, we may consider effect of ionization (and excitation) density in the impingent-particle track. On a simple picture, in slow particle paths, such as are characteristic of about half the phenomena of pile radiolysis, the free atoms and radicals are formed close together by over-all reactions involving rupture of excited molecules either primarily or secondarily produced.[14] They consequently have a better chance to combine to give such products as H_2, CH_4 and C_2H_6 than when they are formed far apart.[15] However, both H_2 and CH_4 may be formed also by attack of radicals on parent molecules, particularly in the side chain,[6,9] so that increased production of C_2H_6 in pile irradiation of the compounds examined could be the principal revelation of this effect. Values of G for C_2 fractions in Table II show such an effect. However, as shown by Table IV, the C_2 fractions are not pure ethane and may, as in the case of toluene, contain no detectable ethane. Thus, we are left with the statement that only $G(C_2)$ values for *t*-butylbenzene may be representative of an ionization density effect. On the other hand, rate of energy input in the pile is smaller by a factor of 100 than in electron irradiations. Thus, if C_2 production is indicative of high concentrations of free methyl, these must be local concentrations such as can be found only in the ionization column.

Increased C_2 production resulting from a Rabino-

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[10] R. R. Hentz, Doctoral Dissertation, University of Notre Dame (1950).

[11] Comparison of C–H and C–C is made between bonds of similar type; *e.g.*, bonds with the ring.

[12] N. Bohr, *Phil. Mag.*, **25**, 10 (1913); **30**, 581 (1915).

[13] H. Bethe, *Ann. Physik*, **5**, 325 (1930).

[14] For discussions of details of the processes *cf.* M. Burton, *Proc. Conf. Nuclear Chem., Chem. Inst. Canada*, 179 (1947); *Ann. Rev. Phys. Chem.*, **1**, 113 (1950); *J. Chem. Ed.*, **28**, 404 (1951); J. L. Magee and M. Burton, THIS JOURNAL, **72**, 1965 (1950).

[15] *Cf.* the Rabinowitch-Wood effect: E. Rabinowitch and W. C. Wood, *Trans. Faraday Soc.*, **32**, 1381 (1936).

witch–Wood effect for pairs of methyl radicals would entail also decreased methane production resultant from action of free methyl on substrate molecules. Table II shows such an expected drop in $G(CH_4)$ in going from electron to pile bombardment. However, except in the case of *t*-butylbenzene where $G(C_2)$ represents largely yield of ethane, we must be cautious in assuming a significant relationship between increase of $G(C_2)$ and decrease of $G(CH_4)$. There is the possibility that increase of $G(C_2)$ reflects increased ring rupture.

Notre Dame, Indiana Received March 2, 1951

[Contribution from the Department of Chemistry, Columbia University]

Rates and Temperature Coefficients in the Hydration of Gaseous Isobutene by Dilute Aqueous Nitric Acid[1]

By Joseph B. Levy, Robert W. Taft, Jr., David Aaron and Louis P. Hammett

We have developed a method for measuring the rate of reaction of a gaseous olefin with an aqueous acid solution from which the rate of reaction of the olefin at unit fugacity may be determined with a probable error of 1% or less, and have applied it to the reaction of isobutene with approximately 0.1 and 1 *m* nitric acid. The energies of activation derived from measurements over a 20° range have a probable error of 0.13 kcal. Because of uncertainties about the distribution constant of olefin between solution and gas phase these rates cannot be directly compared with previous measurements of the rate at unit concentration of dissolved olefin. The rate of reaction at unit fugacity shows an even stronger medium effect than the rate at unit concentration, showing that the effect depends primarily on a sharp variation with acid or salt concentration of the ratio of the activity coefficient of OH_3^+ to the activity coefficient of the likewise positively charged transition state.

A major weakness in present thinking about the problem of structure and reactivity in organic compounds arises from uncertainty about the extent to which the relative reactivity of two substances is determined by other factors than the energy of activation. This is equivalent to uncertainty about the extent to which observed relative reactivities are determined by the accident of the temperature at which measurements are made. The difficulty lies not merely in lack of sufficient data but also in doubts about the validity of existing data which derive from the inherent difficulty of determining energies of activation with sufficient precision. Thus Lucas and co-workers[2] in a valuable study of the acid catalysis of the hydration of olefins to alcohols report without comment data which indicate that in dilute nitric acid isobutene reacts 1.72 times more rapidly than trimethylethylene but that the energy of activation is 4.5 kcal. greater for the more reactive olefin. If these figures are correct the order of reactivity must reverse between 25 and 0° with isobutene less reactive than trimethylethylene at the lower temperature. But the figure of 4.5 kcal. is computed from measurements of four rate constants, one for each of the olefins at each of two temperatures which differ by ten degrees, and a randomly distributed error of only 5% in each of these rate constants would lead to a probable error of 1.8 kcal. in the energy of activation. While it is hardly probable that the energy of activation of isobutene is 0.3 kcal. less than that of trimethylethylene, as must be the case if no reversal of the order of reactivity is to occur at any temperature, it is by no means certain that it is as much as 4.5 kcal. greater. Clearly the temperature coefficients of the hydration reactions of olefins deserve further attention, and we have sought a method of measuring the rate which should be of the highest possible precision. After considering and discarding those used by previous investigators[2,3] we have come to one whose application to isobutene is the subject of the present article.

Principle of the Method.—The method depends upon the drop in the vapor pressure of the volatile olefin from the aqueous solution which accompanies the progress of the reaction. The apparatus was modified from one used by Greenspan, LaMer and Liotta[4] for measuring the rate of evolution of a gas in a constant volume system. We use the symbols

v_1 = volume of acid solution
v_g = volume of gas phase
r = v_g/v_1
p = observed pressure at time t
p_s = partial pressure of the solvent
P = $p - p_s$ partial pressure of gaseous olefin at time t
P^0 = partial pressure of olefin at time 0
P^e = partial pressure of olefin when reaction has reached equilibrium
C_a = concentration of alcohol in solution at time t
C_a^e = concentration of alcohol in solution at equilibrium
C_0 = concentration of olefin in solution at time t
C_0^0 = concentration of olefin in solution at time 0
h = C_0/P the distribution constant of olefin between liquid and gas phases
k_c = rate of conversion of olefin to alcohol in solution at unit concentration of olefin in solution
k_p = rate of conversion of olefin to alcohol in solution at unit pressure of olefin in gas phase; $k_p = k_c h$
k_{-1} = rate of conversion of alcohol to olefin in solution at unit concentration of alcohol in solution
s = $-\mathrm{d}\ln(P - P^e)/\mathrm{d}t$

For this reversible reaction we have, provided equilibrium is at all times maintained in the distribution of olefin between gas and liquid, the basic rate equation

$$\frac{\mathrm{d}C_a}{\mathrm{d}t} = k_c C_0 - k_{-1}C_a = k_p P - k_{-1}C_a \qquad (1)$$

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(1) The work reported herewith was carried out as project NR 056-062 under contract N6onr-271 between the Office of Naval Research and Columbia University. Reproduction in whole or in part permitted for any purpose of the United States Government.

(2) (a) H. J. Lucas and W. F. Eberz, This Journal, **56**, 460 (1934); (b) H. J. Lucas and Yun-Pu Liu, *ibid.*, **56**, 2138 (1934); (c) Yun-Pu Liu and Tien-Chi Wei, *J. Chinese Chem. Soc.*, **4**, 297 (1936).

(3) F. G. Ciapetta and M. Kilpatrick, This Journal, **70**, 639 (1948).

(4) J. Greenspan, V. K. LaMer and S. Liotta, *ibid.*, **59**, 1606 (1937).