tential shift and log K_N appears to be linear, as shown in Fig. 1.

The data in Fig. 1 compare reactions involving two chemical equivalents. This is done because most of the cations being compared are bivalent and their reductions involve two electrons. The reactions involving monovalent cations must therefore be doubled and their equilibrium constants squared in order to conform to this basis. Thus, the value plotted for K_N of Tl^+ is $(10^{0.4})^2 = 10^{0.8}$. *Moreover, the equation of the straight line shown in Fig. 1 has the form of a Nernst equation for a two-electron process and is* $\Delta E_{1/2}(\text{en-aq}) = E' - 0.059/2 \log K_N$. In this equation E' is a constant term which includes both the liquid junction potential and the difference in potential arising from the fact that the electrode reaction at the mercury pool is different in the two solvents. K_N is the over-all stability constant on the basis of two chemical equivalents. A more detailed examination of the thermodynamic significance of this linear relationship will be given in a subsequent paper.

The stability constant of the aqueous lead-ethylenediamine complex has not been previously reported. From Fig. 1, its over-all stability constant may be estimated to be $10^{7.5 \pm 1}$.

Similarly, the square of the stability constant of the cuprous complex can be obtained from Fig. 1 (if the straight line is extended sufficiently) and is $10^{29 \pm 1}$. Thus, its stability constant (which cannot be measured in aqueous solution) is estimated from these polarographic data to be $10^{14.5 \pm 0.5}$.

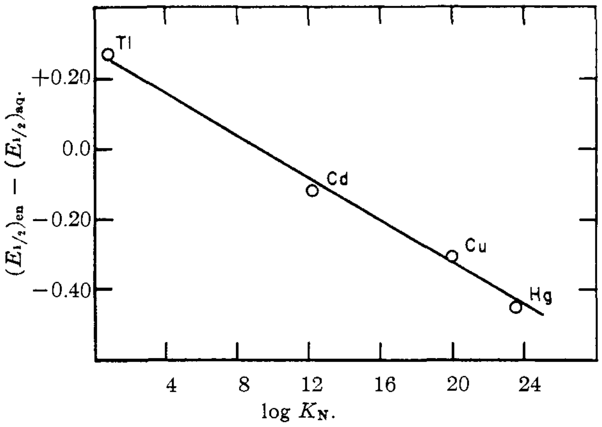

Fig. 1.—Plot of shift in half-wave potentials between ethylenediamine and aqueous solutions for several metal ions *versus* the logarithm of the over-all stability constants of their aqueous ethylenediamine complexes.

Approximate over-all stability constants of other cations with ethylenediamine can be estimated similarly if reversible potentials are known for the reduction of the cations in anhydrous ethylenediamine as a solvent. Furthermore, there seems to be no reason why this method of obtaining approximate over-all stability constants cannot be extended to other liquid solvents whose molecules can serve as coördinating ligands for metal ions.

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BLOOMINGTON, INDIANA

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

The Interaction of β-Particles with Organic Liquids in the Presence of Vinyl Monomers[1]

BY W. H. SEITZER[2] AND A. V. TOBOLSKY

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Solutions of common organic liquids with vinyl monomers (either styrene or methyl methacrylate) have been exposed to a point source of β-particles, and the resulting rates of polymerization were measured for several monomer concentrations. An expression was derived which relates rate of chain initiation to the measured rate of polymerization in terms of the average absorption coefficient for the β-particles. The number of radical chain starters produced in the various organic liquids per 100 e.v. of energy absorbed was thereby calculated.

One method of studying the effects of high energy β-particles on organic liquids is to allow the resulting fragments to react with a known concentration of an active substance which undergoes a simple and measurable chemical change. In the experiments here reported the active substance is a vinyl monomer, either styrene or methyl methacrylate, which polymerized under these conditions. Various concentrations of monomer in organic liquids have been irradiated by placing a source of pure β-radiation in the center of a spherical container having a diameter large enough to stop all of the particles. The resulting rates of polymerization of the monomers have been measured.

The Source.—The source of radiation was an equilibrium mixture of Sr^{90} and Y^{90} chlorides deposited in a thin glass bulb 3 mm. in diameter. The bulb was blown on the end of a 1 mm. diameter capillary, the other end of which was ring-sealed to a 7/25 standard taper joint. This apparatus was inserted into a spherical flask in such a manner that the bulb was in the center of the flask.

Both Sr^{90} and Y^{90} are pure β-emitters with energies of 0.61 and 2.24 Mev., respectively. The half-life of Sr^{90} is 19.9 years. By measuring the activity of an aliquot portion, the total activity of these isotopes in the bulb was estimated to be 1.74×10^{10} counts/min. The average thickness of the glass bulb was shown from absorption measure-

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[1] This article is based upon a dissertation submitted by W. H. Seitzer in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Princeton University. Allied Chemical and Dye Corporation Fellow, 1952–1953; General Electric Company Fellow, 1953–1954.

[2] Sun Oil Company Laboratories, Norwood, Pennsylvania.

ments to be 6.40 mg./cm.^{2} A β-spectrometer was used to measure the spectra at various absorber thicknesses, and from these was calculated the average energy per particle as a function of absorber thickness.[3] The value corresponding to 6.40 mg./cm.^{2} was shown to be 0.584 Mev. per particle. After suitable allowances were made for the loss of particles entering the stem of the bulb it was found that the source emitted $8.47 \times 10^9 \pm 0.94 \times 10^9$ Mev./min.

Experimental Procedure

Materials.—Dow Chemical Company N-99 styrene was given a one-plate distillation under nitrogen at 10 mm. pressure to remove the inhibitor. Only the center fraction boiling over a 0.1° range was used. Rohm and Haas Company methyl methacrylate was washed with 5% NaOH to remove the inhibitor, dried over potassium carbonate and distilled under nitrogen at 100 mm. pressure. The center portion, with a boiling range of 0.2°, was used.

Mallinckrodt Chemical Works analytical reagent benzene was used without further purification. Low sulfur carbon tetrachloride from the Mallinckrodt Chemical Works was used without further purification. Baker and Adamson reagent grade ethyl bromide was washed with concentrated sulfuric acid, sodium carbonate solution and water; after drying over calcium chloride the material was given a simple distillation; the center fraction being retained. Ethyl iodide from the Mathieson Company was bleached with a dilute solution of sodium thiosulfate, dried and simply distilled, retaining the center fraction which was stored over mercury until used. Mallinckrodt Chemical Works analytical reagent chloroform was used without further purification; it was found experimentally that the preservative, ethyl alcohol, had no observable effect on the results. Carbide and Carbon Company technical grade acetone was distilled from the sodium iodide complex; this product was shaken with AgOH, dried and fractionated in a 10-plate column. Eastman Kodak Company white label toluene (sulfur free) was dried and fractionated in a 10-plate column. Mathieson Company cyclohexane was shaken with nitrating acid, dried and fractionated. Carbide and Carbon Company technical grade dioxane was refluxed with 10% HCl, allowed to stand over KOH pellets for 24 hours, and fractionated over sodium; the product was again fractionated over sodium immediately before using.

Apparatus.—The solution of monomer and solvent was placed in a spherical flask with a radius of 12.4 mm., and a total volume of approximately 8 ml. This thickness of solution was in most cases great enough to absorb all of the particles emanating from the centrally-located source. (The range of a 2.24 Mev. β-particle[3] is 1.020 g./cm.^{2}.) In the case of solvents, such as acetone and dioxane, with densities less than styrene, it was shown that the effect of incomplete absorption was negligible.

Method.—The necessary quantity of monomer solution (8 ml.) was pipetted into the flask. After inserting the source, the solution was degassed twice by freezing with liquid nitrogen and evacuating with an oil pump. After the final freezing, the side-arm was sealed and the apparatus placed in a water thermostat at 30.5°. The polymer was precipitated by pouring the diluted solution slowly into a 10-fold excess of methyl alcohol. The filtered polymer was dried in a vacuum oven at 60° and weighed. Identical polymerizations in the absence of β-radiation were carried out for the purpose of obtaining the thermal rate of polymerization.

It was found necessary to exclude light from some mixtures of solvents and monomers to prevent photo polymerization. Solutions containing dioxane, ethyl iodide or ethyl bromide were found to give abnormally high rates in the presence of light; therefore, light was excluded by wrapping the reaction flasks with aluminum foil.

In all cases the β-ray initiated polymerization was allowed to proceed to about 1% conversion. For styrene the necessary time for this amount of conversion was on the order of two days. For methyl methacrylate an equivalent conversion occurred in about four hours.

Experimental Results

Proof of Radical Initiation.—It was previously shown and reported[4] that the initiation of polymerization by β-radiation proceeds by a radical mechanism. A polymerization was carried out by exposing an equimolar mixture of styrene and methyl methacrylate to the β-source. Analysis of the resulting copolymer showed it to be an approximately equimolar mixture of the two monomers. Walling, *et al.*,[5] have shown that this is typical behavior for a radical initiator as opposed to cationic or anionic initiators which give a polymer composed of nearly 100% styrene or 100% methyl methacrylate, respectively.

This proof of radical type polymerization is reported by the fact that oxygen is a powerful inhibitor. In addition the measured degree of polymerization for each monomer is approximately equal to that calculated from the monoradical line.[4,6]

Rates of Polymerization in Solvents.—Tables I and II show the results for rate of polymerization in moles per second when mixtures of organic solvents and monomers in various concentrations were exposed to β-rays in the apparatus described above. The rate values shown are the average of one to eight runs at the specific concentrations. Each solvent was mixed with monomer in ratios of 1:3, 1:1, 3:2 and 3:1 by volume. The tables list the corresponding solvent to monomer ratios at 30°. The reproducibility of the polymerization rate is somewhat variable, the scatter of experimental results being greater for some systems and less for others. For example, the results with the two pure monomers are shown in Table III. The maximum deviation from the mean was, in general, not greater than about 10%.

The tabulated values for the rate of polymerization in moles/sec. given in the third column of Tables I and II were obtained from the formula[6]

$$W_\infty = ([W(\text{obs.})]^2 - [W(\text{th})]^2)^{1/2}$$

where W_∞ is the tabulated value, W(obs.) was the experimentally observed rate obtained in the presence of β-rays, and W(th) was the thermal rate under the same conditions. In dilute solutions of monomer W_∞ was essentially equal to W(obs.). In no case did W_∞ and W(obs.) differ by more than 10%.

The calculation of the rate of polymerization involved the assumption that the conversion was linear with time. This assumption was tested and seemed to be valid within the experimental error (see Table III).

Preliminary tests were run on some other solvents in addition to those in the tables. Solutions containing up to 2% by weight of *t*-butyl peroxide gave approximately the same rate of polymerization as pure monomer at 30°. The same is true for both $SnCl_4 \cdot 5H_2O$ and glacial acetic acid. Sublimed carbon tetrabromide seemed to give an inhibitory effect. A 5% solution of titanium tetrachloride in methyl methacrylate gave no observed polymerization in the ordinary time.

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[3] R. H. Goeckermann and W. H. Seitzer, *J. Chem. Phys.*, **20**, 1655 (1952).

[4] W. H. Seitzer, R. H. Goeckermann and A. V. Tobolsky, THIS JOURNAL, **75**, 755 (1953).

[5] C. Walling, E. R. Briggs, W. Cummins and F. R. Mayo, *ibid.*, **72**, 48 (1950).

[6] D. H. Johnson and A. V. Tobolsky, *ibid.*, **74**, 938 (1952).

TABLE I

RESULTS OF SOLVENTS AND STYRENE

Solvent	[S]/[M]	$W_\infty \times 10^9$, moles/sec.	ρ, g./cc.	$\rho^4\, 2A'/[M]^3 (W_\infty)^2 \times 10^{16}$
None	0	3.35	0.897	1.02
Carbon tetrachloride	0.396	8.58	1.085	39.3
	1.18	5.34	1.273	101
	1.78	4.13	1.348	143
	3.560	2.10	1.461	210
Chloroform	0.475	7.58	1.041	25.8
	1.42	4.29	1.183	46.8
	2.13	3.82	1.241	88.2
	4.28	1.83	1.326	108
Ethyl bromide	0.52	3.64	1.033	5.84
	1.58	2.10	1.168	10.72
	4.76	1.03	1.303	33.84
Ethyl iodide	0.474	4.99	1.151	16.85
	1.42	2.80	1.404	26.07
	2.13	1.92	1.506	48.51
	4.27	0.80	1.658	77.08
Benzene	0.429	3.43	0.890	2.85
	1.28	2.55	.882	5.14
	1.93	1.82	.880	5.08
	3.86	1.26	.875	9.74
Toluene	0.360	3.15	.887	2.27
	1.07	1.93	.876	2.34
	1.61	1.87	.873	3.85
	3.24	1.22	.866	6.41
Cyclohexane	0.354	3.49	.865	2.63
	1.05	2.54	.833	4.07
	1.590	2.71	.821	8.52
	3.18	1.75	.801	12.7
Acetone	0.517	5.91	.867	7.63
	1.55	3.85	.837	9.23
	2.35	3.04	.826	10.9
	4.66	1.55	.812	10.9
Dioxane	0.448	4.50	.929	5.18
	1.34	3.32	.959	12.1
	2.01	2.37	.972	12.8
	4.04	1.74	.991	30.6

TABLE II

RESULTS OF SOLVENTS AND METHYL METHACRYLATE

Solvent	[S]/[M]	$W_\infty \times 10^9$, moles/sec.	ρ, g./cc.	$\rho^4\, 2A'/[M]^3 (W_\infty)^2 \times 10^{16}$
None	0	52.95	0.933	14.2
Carbon tetrachloride	0.367	40.5	1.112	39.9
	1.09	23.6	1.291	84.2
	1.64	17.6	1.362	111
	3.29	11.4	1.470	263
Chloroform	0.438	40.7	1.068	34.4
	1.31	22.6	1.201	56.9
	1.99	15.3	1.255	60.8
	3.96	10.8	1.335	159
Ethyl bromide	0.490	29.1	1.060	17.0
	1.46	15.6	1.180	25.1
	2.20	9.86	1.237	23.8
	4.40	6.10	1.312	47.2
Ethyl iodide	0.438	34.2	1.178	3.60
	1.31	26.0	1.422	147.8
	1.92	10.7	1.520	64.1
	3.94	4.24	1.667	59.4
Benzene	0.397	42.3	0.919	20.3
	1.19	20.5	0.900	14.7
	1.68	16.0	.894	17.1
	3.57	6.88	.884	12.4
Acetone	0.479	41.6	.894	17.6
	1.43	27.6	.855	21.7
	2.15	23.0	.840	27.6
	4.31	12.4	.816	29.9
Dioxane	0.415	40.8	.956	22.1
	1.24	28.0	.977	38.1
	1.86	22.2	.986	48.8
	3.73	13.3	1.000	76.6

TABLE III

Run	Hr.	Polymer, mg.	Mg./hr.
		Styrene	
1	24.0	32.1	1.33
6	24.0	29.8	1.24
35	38.0	52.7	1.39
302	47.8	57.1	1.20
4	48.0	53.4	1.11
		Av.	1.25
		Methyl methacrylate	
303	2.6	49.2	19.0
306	2.7	50.6	19.0
307	4.0	79.3	19.8
29	6.0	121.5	20.2
32	6.0	108.6	18.1
30	11.0	208.0	18.9
		Av.	19.2

Mixed Solvents.—In order to test the effect of mixing solvents a solvent composed of benzene and carbon tetrachloride in various proportions was mixed with monomer and exposed to β-radiation. Table IV gives the results. Here again the proportions of mixed solvent to monomer are 1:3, 1:1, 3:2 and 3:1 by volume

Water.—In view of the interest in irradiation of water solutions, some preliminary tests were made to ascertain the effect of water on the experiments reported here. Styrene and methyl methacrylate saturated with water gave no measurable difference in polymerization rate as compared to perfectly dry monomers. The same is true for solutions of acetone and methyl methacrylate containing water up to a concentration of one part water to ten parts acetone (by volume). However, addition of water to dioxane gave an effect which appears to be outside experimental error. Unfortunately, the range of water concentration is very small due to the fact that at moderate concentrations two phases are formed when methyl methacrylate is added. Table V lists the data obtained from varying the water concentration in a 3:2 solvent–methyl methacrylate solution. The high rates obtained in this case may be due to a decrease in termination rates as a result of tighter coiling of the polymer radicals in the poor solvent.

Theory for a Point Source.—The theory for homogeneous radical initiation of vinyl polymerization has been developed[6,7] so that the rate of initiation can be calculated from the measured rate of polymerization. This calculation requires extension for the case of an inhomogeneous polymerization such as that effected by β-rays. We shall now derive an expression by which the rate of initiation of polymer chains can be calculated from the ex-

(7) A. V. Tobolsky and B. Baysal, *J. Polymer Sci.*, **11**, 471 (1953).

TABLE IV

POLYMERIZATION USING A MIXTURE OF BENZENE AND CARBON TETRACHLORIDE

Solvent	Monomer concn., moles/l.	CCl_4 concn., moles/l.	Benzene concn., moles/l.	Rate of polymerization, moles/sec. × 10^9
	Styrene			
1:2 CCl_4 and benzene	6.46	0.85	1.85	9.85
	4.31	1.71	3.70	6.20
	3.44	2.05	4.44	4.27
	2.15	2.56	5.55	2.58
1:1 CCl_4 and benzene	6.46	1.28	1.39	8.75
	4.31	2.56	2.78	6.20
	3.44	3.07	3.33	4.72
	2.15	3.84	4.16	2.50
	Methyl methacrylate			
1:2 CCl_4 and benzene	6.99	0.85	1.85	43.1
	4.66	1.71	3.70	35.5
	3.72	2.05	4.44	27.7
	2.33	2.56	5.55	15.0
1:1 CCl_4 and benzene	6.99	1.28	1.39	54.4
	4.66	2.56	2.78	35.0
	3.72	3.07	3.33	23.8
	2.33	3.84	4.16	13.8
2:1 CCl_4 and benzene	6.99	1.71	0.92	45.0
	4.66	2.81	1.85	25.2
	3.72	4.09	2.22	16.7

TABLE V

POLYMERIZATION USING A 3:2 MIXTURE OF WATER–DIOXANE AND METHYL METHACRYLATE

Water concn., moles/l.	Dioxane concn., moles/l.	Monomer concn., moles/l.	Rate of polymerization, moles/sec. × 10^9
0.0	7.01	3.73	22.2
1.06	6.88	3.68	26.8
2.34	6.71	3.57	28.2
3.14	6.62	3.52	29.6
4.11	6.50	3.45	30.6

perimentally determined amount of polymer formed per unit time. The derivation applies for the experimental system described previously, *i.e.*, a source surrounded by a spherical volume of solution sufficient to absorb all of the radiation. Since the absorption of β-particles is approximately exponential, the rate of initiation (and, therefore, the rate of polymerization) must vary as the distance from the source.

It is convenient to use the concept of total rate of initiation I_{nit}, *i.e.*, the total number of polymer chains initiated per unit time in the entire volume under consideration. In terms of the customary notation for the homogeneous theory

$$I_{nit} = R_i V \tag{1}$$

where R_i is the rate of initiation per unit volume and V is the volume. Because of the uncertainty in the termination step, new terms I_{nit}' and R_i are defined such that

$$I_{nit}' = I_{nit}(1 + x)$$
$$R_i' = R_i(1 + x)$$

where x is the proportion of termination by disproportionation and can vary from zero to unity. This notation is thoroughly discussed in an earlier paper.[7] It was shown that for homogeneous polymerization

$$R_i' = \frac{2A'}{[M]^2} R_p^2 \tag{2a}$$

where R_i and R_p are rates of initiation and polymerization in mole/l./sec., [M] is monomer concentration and A' is the slope of the monoradical line.[6] In this paper it will be more convenient to use units of cc. rather than liters. Equation 2a then becomes

$$R_i' = \frac{2A'}{[M]^2} \times 10^3 R_p^2 \tag{2b}$$

where R_i' and R_p are in moles/cc./sec. The constant A' has the same numerical value and the same dimensions as in equation 2a.

We define a new quantity W, the total rate of polymerization in the entire volume V. For homogeneous polymerization in a spherical volume of radius r

$$W = R_p V = R_p \times 4/3\pi r^3 \tag{3}$$

From equation 1 and 2

$$I_{nit}' = \frac{2A'}{[M]^2} \times 10^3 \times \frac{(W)^2}{V} \tag{4}$$
$$= \frac{2A'}{[M]^2} \times 10^3 \times \frac{W^2}{4/3\pi r^3}$$

where V is in cc. and r is in cm. It will be shown that the proper expression for the total inhomogeneous initiation caused by a point source of β-rays in the center of an infinite sphere is

$$I_{nit}' = \frac{\alpha^3\rho^3}{0.064\pi} \times \frac{2A'}{[M]^2}(W_\infty)^2 \tag{5}$$

where α is the average absorption coefficient of the β-particles in cm.^{2}/g., ρ is the density of the medium, and W_∞ is the total rate of polymerization over the entire volume.

For conceptual purposes we can calculate the total rate of initiation produced by β-rays by making the fictitious assumption that the total rate of polymer formation W_∞ occurs homogeneously within a sphere of radius r_m. By comparing equations 4 and 5 we find that $r_m = 3.63/\alpha$. For the $Sr^{90} - Y^{90}$ source that was used in this work, and for a medium of density unity, the maximum range R is 1.020 cm.[3]. Using the value of $\alpha = 4.7$ cm.^{2}/g. for our β-ray source, we obtain a ratio $r_m/R = 0.756$.

In order to derive expression (5) the fundamental assumption is made that the rate of initiation by β-radiation in a spherical shell of volume dV is proportional to the loss of energy in that shell

$$dI_{nit} = -k\, dE \tag{6}$$

where k is a proportionality constant depending on the absorbing substance and E is energy entering the surface of a sphere with a radius r. The exponential absorption law states[8]

$$dE = -\lambda E\, dr \tag{7}$$

where λ is the absorption coefficient in cm.$^{-1}$. Combining equation 6 and 7 gives

$$dI_{nit} = k\lambda E\, dr \tag{8}$$

Since $dI_{nit} = R_i\, 4\pi r^2 dr$, it can be shown easily that R_i at any radius r is

$$R_i = \frac{k\lambda E_0 \exp(-\lambda r)}{4\pi r^2} \tag{9}$$

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[8] G. Friedlander and J. Kennedy, "Introduction to Radiochemistry," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 158.

where E_0 is the total energy emanating from the source.

If $\mathrm{d}W = R_p\,\mathrm{d}V$, it can be shown by introducing equations 2 and 4 that

$$\mathrm{d}W = \left(\frac{4\pi k\lambda E_0}{K}\right)^{1/2} r \exp\left(-\frac{\lambda r}{2}\right)\mathrm{d}r \qquad (10)$$

where K is $2A' \times 10^3/[(\mathrm{M})^2(1 + x)]$. If the radius is greater than the maximum range of the β-particles, all of the energy will be absorbed. This compares with r going to infinity in the exponential function. Integrating $\mathrm{d}W$ from zero to infinity

$$W_\infty = \left(\frac{4\pi k\lambda E_0}{K}\right)^{1/} \frac{4}{\lambda^2} \qquad (11)$$

As a first approximation for organic liquids, the range of β-particles is dependent only upon the density of the medium. Thus, there exists an absorption coefficient α in cm.²/g. which is common for most solvents. Since $\lambda = \alpha\rho$, equation 11 becomes

$$\rho^3 \frac{2A'}{[\mathrm{M}]^2}(W_\infty)^2 = \frac{0.064\pi k E_0}{\alpha^3}(1 + x) \qquad (12)$$

Integration of equation 6 from $r = 0$ to $r = \infty$ gives

$$I_{\mathrm{nit}} = kE_0 \qquad (13)$$

$$I_{\mathrm{nit}}' = \frac{\alpha^3\rho^3}{0.064\pi}\frac{2A'}{[\mathrm{M}]^2}(W_\infty)^2 \qquad (14)$$

It is assumed that diffusion and convection do not alter the spatial distribution of radicals so that polymerization occurs exactly at the site of the initiation. In order to calculate the rate of initiation from the rate of polymerization by means of equation 14 it is necessary to know the value of the absorption coefficient. This value is 4.71 cm.²/g. as tabulated by Siri[9] for the linear absorption of particles from Y^{90}. (It is assumed that the suggestion of Rossi and Ellis[10] is correct, namely, that α is in units of cm.²/g. rather than cm.²/mg.). Analysis of the β-spectrum[2] of $Sr^{90} - Y^{90}$ at 6.40 mg./cm.² of absorber shows that about 23% of the total energy comes from the Sr^{90} disintegrations, while the remaining 77% is due to Y^{90}. One would, therefore, expect that the average absorption coefficient of $Sr^{90} - Y^{90}$ should be rather close to the value of the absorption coefficient of Y^{90}.

Extension of the Theory to Multi-component Systems.—For multicomponent systems the assumption is made that the interaction of β-particles with any component is independent of the other components. Equation 13 then becomes

$$I_{\mathrm{nit}} = E_0 \sum k_i w_i \qquad (15)$$

where w_i is the weight fraction of the iᵗʰ component. For a pure substance the rate of initiation is simply kE_0 since the weight fraction then becomes unity. Equation 12 can similarly be altered for a multicomponent system by substituting $k_i w_i$ for k. In the special case of a system composed of solvent and monomer equation 12 becomes

$$\frac{2A'}{[\mathrm{M}]^3}\rho^4(W_\infty)^2 = K_\mathrm{M} + K_\mathrm{S}\frac{[\mathrm{S}]}{[\mathrm{M}]} \qquad (16)$$

where $K_\mathrm{M} = 6.4 \times 10^{-5}\,\pi M_\mathrm{M}\,\alpha^{-3}k_\mathrm{M}E_0(1 + x)$ and $K_\mathrm{S} = 6.4 \times 10^{-5}\,\pi M_\mathrm{S}\,\alpha^{-3}k_\mathrm{S}E_0(1 + x)$, M_M and M_S are molecular weights of monomer and solvent, respectively, and [M] and [S] are monomer concentration and solvent concentration in moles per liter. A plot of $2A'/[\mathrm{M}]^3\,\rho^4\,(W_\infty)^2$ *versus* [S]/[M] should give a straight line with a slope of K_S and an intercept of K_M. Since α has been measured it is possible to calculate $I_{\mathrm{nit}'} = I_{\mathrm{nit}}\,(1 + x)$ from the formula

$$I_{\mathrm{nit}}' = \left(\frac{K_\mathrm{M}}{M_\mathrm{M}}w_\mathrm{M} + \frac{K_\mathrm{S}}{M_\mathrm{S}}w_\mathrm{S}\right)\frac{10^5\alpha^3}{6.4\pi} \qquad (17)$$

where M_M is the molecular weight of monomer and M_S the molecular weight of solvent.

For pure monomer equation 17 becomes

$$I_{\mathrm{nit}}' = \frac{K_\mathrm{M}}{M_\mathrm{M}}\frac{10^5\alpha^3}{6.4\pi} \qquad (18)$$

Similarly we can *define* I_{nit}' for the pure solvent as

$$I_{\mathrm{nit}}' = \frac{K_\mathrm{S}}{M_\mathrm{S}}\frac{10^5\alpha^3}{6.4\pi} \qquad (19)$$

Calculation of Rates of Initiation.—The experimental data have been used to calculate $(2A'/[\mathrm{M}]^3)\,\rho^4(W_\infty)^2$ for the various solvents. The densities were calculated from existing data in the "International Critical Tables," assuming no change in volume upon mixing. The results for $(2A'/[\mathrm{M}]^3)\,\rho^4(W_\infty)^2$ *versus* [S]/[M] are listed in Tables I–II, and a few sample plots are shown in Figs. 1 and 2, namely for the solvents CCl_4, $CHCl_3$ and dioxane in styrene and methyl methacrylate. Many of the plots of $(2A'[\mathrm{M}]^3)\rho^4(W_\infty)^2$ *versus* [S]/[M] have much more scatter than those shown in Figs. 1 and 2. However, the only possible curves connecting the scattered points appear to be straight lines in all cases except for the system styrene–acetone. We have no explanation for this last result, particularly since the system methyl methacrylate–acetone gives a straight line in this type of plot.

The Efficiency of Energy Utilization.—As was previously indicated, the slopes and intercepts of the lines obtained in these plots are the values of K_S and K_M, as seen in equation 16. These values are tabulated for both monomers and for the various solvents in Table VI. Some solvents have two K_S values, one obtained in each monomer. It is gratifying that the K_S values for *most* of the solvents studied are quite similar for both monomers. This is a partial justification for the assumption of additivity inherent in equation 3. In these cases an average K_S for the solvent in both monomers is given in Table VI. The values of $I_{\mathrm{nit}'}$, the rate of production of radicals effective as chain starters, were calculated from equations 6 and 7 and also tabulated.

In two cases, those of benzene and dioxane, the values of K_S were somewhat different in both monomers. The value of K_S for benzene in methyl methacrylate may be inaccurate because the much higher rate of initiation in methyl methacrylate tends to obscure the contribution of the benzene.

In the case of dioxane, it may be that dioxane–methyl methacrylate forms a weak complex so that the assumption of additivity inherent in equation 3 is no longer correct.

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[9] W. E. Siri, "Isotopic Tracers and Nuclear Radiation; with Applications to Biology and Medicine," McGraw-Hill Book Co., New York, N. Y., 1949, p. 73.

[10] H. H. Rossi and R. A. Ellis, Jr., *Nucleonics*, **7**, [1] 18 (1950).

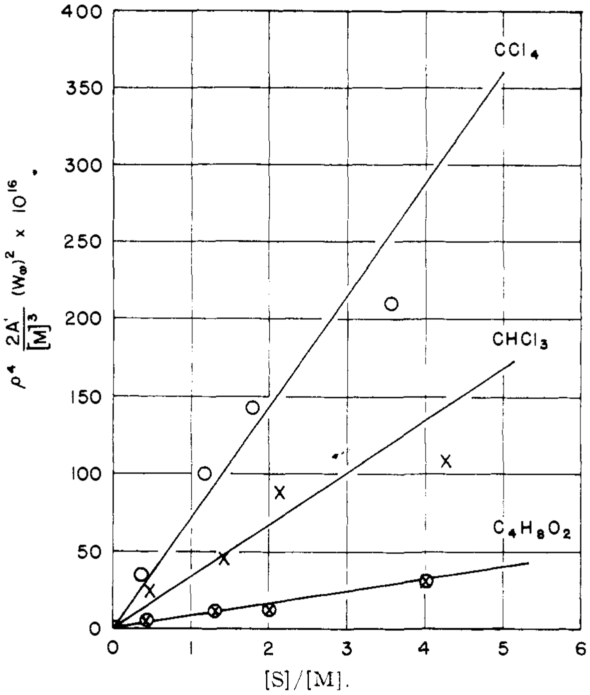

Fig. 1.—Styrene and solvents.

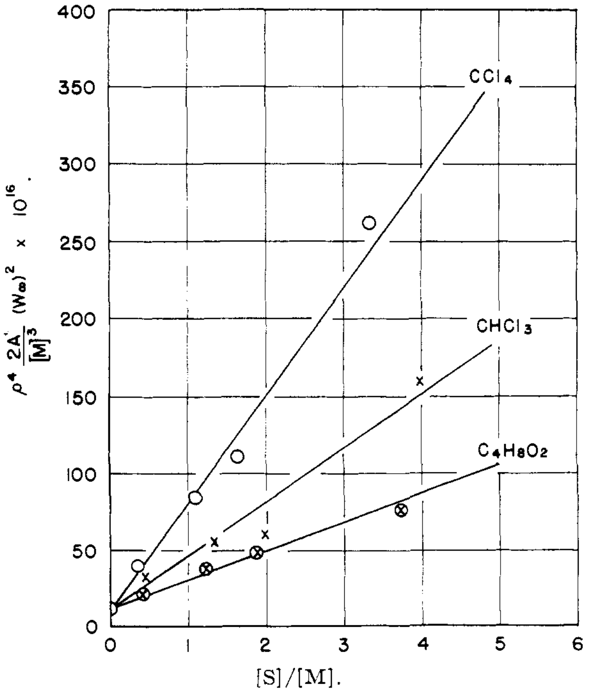

Fig. 2.—Methyl methacrylate and solvents.

The fact that the assumption of additivity is not valid in all cases is shown by the data of Table IV where rates of polymerization are higher in mixed CCl_4 and benzene than with either solvent alone.

TABLE VI

THE EFFICIENCY OF ENERGY UTILIZATION

Solvent	$K \times 10^{16}$ styrene	$K \times 10^{16}$ methyl methacrylate	Av. $K \times 10^{16}$	Av. $I_{nit'} \times 10^{12}$, moles/sec.	Av. G radicals per 100 e.v.
Styrene	1.02	...	1.02	0.513	0.220
Methyl methacrylate	...	14.2	14.2	7.36	3.14
Carbon tetrachloride	71.4	69.2	70.3	23.8	10.2
Chloroform	33.6	34.5	34.0	14.9	6.49
Ethyl bromide	7.14	7.36	7.25	3.60	1.54
Ethyl iodide	20.0	18.2	19.1	6.36	2.72
Benzene styrene	2.67	...	2.67	1.78	0.76
Benzene in methyl methacrylate		1.2	1.2	0.80	0.34
Toluene	1.68	...	1.68	0.94	0.40
Cyclohexane	3.66	...	3.66	2.28	0.96
Acetone	...	6.24	6.24	5.59	2.38
Dioxane in styrene	7.88	...	7.88	4.66	2.01
Dioxane in methyl methacrylate		18.4	18.4	10.9	4.65

If the rate of initiation $I_{nit'}$ is divided by the total energy absorbed, an efficiency of energy utilization can be calculated. It has been shown in Section I that the total energy is 8.47×10^9 Mev./min. The efficiency G in radicals effective as chain starters produced per 100 e.v. absorbed is shown in the last column in Table VI.

Discussion

The results for the solvents indicate that halogen containing compounds are more sensitive to β-radiation than any of the other compounds tested. Fewer halogen atoms per molecule give less sensitivity. Iodine atoms are more sensitive than bromine atoms. Hydrocarbons are the least efficient. Aromatics are less efficient than aliphatics. The other functional groups—esters and ethers—lie about at the same level of efficiency as single halogen atoms.

This relative sensitivity agrees very well with the results for γ-radiation obtained by Prevost-Bernas and co-workers.[11] A comparison with the absolute efficiencies these workers obtained with γ-radiation shows that the G values are about 9 times greater than those obtained here for β-radiation. This large difference cannot be explained by the estimated error in the present work. Until further work is done on this problem, the authors must conclude that production of radicals in organic solvents is more efficient by gamma than beta radiation. The reason for this phenomenon is not clear.

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[11] A. Prevost-Bernas, A. Chapiro, C. Cousin, Y. Landler and M. Magat, *Disc. Faraday Soc.*, **12**, 98 (1952).