TABLE II

LABELING BY EXPOSURE TO TRITIUM GAS

Compound	Quantity, g.	Tritium, curies	Exposure time, days	Activity, mc./g. Crude	Activity, mc./g. Pure
p-Dichlorobenzene	0.525	1.5	3	44	32
Naphthalene	1.0	3.4	0.8	28	7.2
Palmitic acid	20	10.4	11	41	15

TABLE III

LABELED BY-PRODUCTS FORMED IN THE ELECTRIC DISCHARGE AND GAS EXPOSURE TECHNIQUES

By-product	Relative tritium content, parent compd. = 100 Discharge	Relative tritium content, parent compd. = 100 Gas exposure
From dichlorobenzene:		
Chlorobenzene	68	26
Benzene	87	1
Hydrocarbons, $<C_6$	39	..
Other[a]	..	8
From naphthalene:		
Tetrahydronaphthalene	17	23
trans-Decalin	9	..
Alkylbenzenes[b]	57	..
Benzene	28	3
Hydrocarbons, $<C_6$	71	3

[a] Unidentified product less volatile than dichlorobenzene.
[b] Including toluene, ethylbenzene and butylbenzene.

naphthalene is considerably lower, amounting to 2 micromoles. On this basis the decomposition of the organic compound can be estimated to be certainly less than 0.1%, a conclusion which is consistent with the failure to observe chemical decomposition products by conventional analysis in the vapor fractometer. It seems reasonable to assume, since chemical decomposition was undetectable by vapor fractometry and since a reservoir of tritium remains after the discharge times used, that even higher levels could be attained by prolonging the discharge.

TABLE IV

DISCHARGE IN DEUTERIUM–NAPHTHALENE

Wt. $C_{10}H_8$, g.	Discharge time, min.	Pressure, mm. Initial	Pressure, mm. Final	Final gas composition[a] D_2	Final gas composition[a] HD	Final gas composition[a] H_2
0.535	5	12.2	11.0	81.7	16.6	1.6
0.501	5	14.1	13.2	83.1	12.7	1.6

[a] Initial composition: $D_2 = 99\%$, $HD = 1\%$.

It appears, from a consideration of the fact that the discharge has effectively produced labeling at pressures as high as 13 mm., at which pressure the mean free path in the gas is less than 5×10^{-4} cm., that the process does not likely depend solely upon accelerated tritium ions. The complexities of a Tesla discharge, however, are so great that this conclusion cannot be reached with certainty from the present experiments. A definitive answer to this question will have to come from experiments with a steady-state glow discharge, along with a determination of the labeling yields in such a discharge.

Labeling would be expected to occur as a result of the primary processes of ionization, excitation and dissociation of the tritium molecules in the gas phase. Following this, hydrogen abstraction from the organic compound and subsequent combination with tritium atoms, or abstraction by the organic free radical of a tritium atom from the gaseous molecule would lead to a labeled compound. Ionization and excitation of the compound by the discharge also may be involved. The data obtained furnish no basis for any more extensive discussion of mechanism.

DETERMINATION OF FREE RADICAL YIELDS IN THE RADIOLYSIS OF MIXTURES BY THE POLYMERIZATION METHOD

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Radiation initiated solution polymerization of vinyl monomers can be used as a method for investigating the radiolysis of binary mixtures. In such systems the monomer is one of the components of the mixture and at the same time acts as a free radical scavenger. The rate of free radical production in the system can be derived from polymerization rates provided the rate constants for chain propagation and termination are known. A number of systems have been examined. In the most simple case the rate of free radical production is a linear function of chemical composition of the mixture. This situation applies to styrene solutions in aromatic hydrocarbons and to methyl methacrylate and vinyl acetate solutions in methyl and ethyl acetate. Other systems however exhibit "protection" and sensitization effects. These results are discussed on the basis of current theories for the kinetics of energy transfer processes. Free radical yields are derived from all available data and the results are compared with yields obtained by other methods.

I. Introduction

The interest of radiation chemists has been focussed in recent years on the radiolysis of binary mixtures. In such systems energy transfer processes often are observed which lead to non-linear relationships between product yields and the chemical composition of the mixture. Observations along these lines were made by measuring gas evolution in the radiolysis of a number of mixtures,[1-3] disappearance of diphenylpicrylhydrazyl (DPPH),[4-6] reaction with mercaptans[7] and polymer degrada-

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(1) J. P. Manion and M. Burton, THIS JOURNAL, **56**, 560 (1952).

(2) S. Gordon and M. Burton, *Faraday Soc. Disc.*, **12**, 88 (1952).

(3) W. N. Patrick and M. Burton, THIS JOURNAL, **58**, 421 (1954).

(4) L. Bouby and A. Chapiro, *J. chim. phys.*, **52**, 645 (1955).

(5) L. Bouby, Thesis, University of Paris, 1957.

(6) M. Magat, L. Bouby, A. Chapiro and N. Gislon, *Z. Elektrochem.*, **62**, 307 (1958).

(7) T. D. Nevitt, W. A. Wilson and H. S. Seelig, 131st A.C.S. Meeting, Miami, April 1957.

tion in solution.[8] Direct evidence for the existence of energy transfer processes in irradiated liquids was gained from studies on radiation induced luminescence in various solutions.[9-10]

Another method for investigating the radiolysis of binary mixtures is based on kinetic studies of radiation-initiated polymerizations of vinyl monomers in solution.[11-16] In such systems the vinyl monomer is one of the components of the mixture and at the same time acts as a free radical scavenger. The rate of polymerization is directly related to the rate of free radical production in the mixture and hence the primary free radical yields can be determined. Since the process involved here is a chain reaction, the ratio of rate constants for chain propagation and termination must be accurately known and furthermore only mixtures in which the reaction follows normal kinetic behavior can be investigated by this method. These requirements are best fulfilled for styrene, methyl methacrylate and vinyl acetate solutions in substances which also dissolve the corresponding polymer, since it is well established that anomalous kinetic features occur when polymerization takes place in heterogeneous media.[11] Several attempts already have been made to determine free radical yields by this method. In earlier work[11-14] it was assumed that a simple additivity rule was governing free radical yields in binary mixtures. This assumption was however found to hold only in a few special cases and more often energy transfer processes were operative.[15-16] The present article is an attempt to correlate all available data in this field and to examine the validity of this method and also its limitations. Experimental material is collected from both earlier publications and unpublished work from this Laboratory.

II. Basic Kinetic Equations

When a vinyl monomer is radiation polymerized in solution at ordinary temperatures, the reaction is initiated usually by free radicals R· originating from the radiolysis of both the monomer M and the solvent S. The propagation step proceeds in the conventional manner and, provided the radiation dose-rate is not too high and the monomer concentration is large enough to trap all primary radicals, termination occurs exclusively by the bimolecular interaction of two growing chains. This leads to the conventional kinetic scheme of free radical polymerizations

$$\begin{array}{lll} & \text{rates} & \\ \mathrm{M} \rightsquigarrow \mathrm{R}\cdot & \left.\begin{array}{l}\varphi_{\mathrm{M}} I(\mathrm{M}) \\ \varphi_{\mathrm{S}} I(\mathrm{S})\end{array}\right] R_{\mathrm{i}} & \begin{array}{l}(1)\\(2)\end{array} \\ \mathrm{S} \rightsquigarrow \mathrm{R}\cdot & & \\ \mathrm{R}\cdot + \mathrm{M} \longrightarrow \mathrm{RM}\cdot & & (3) \\ \mathrm{RM}_n\cdot + \mathrm{M} \longrightarrow \mathrm{RM}_{n+1}\cdot & k_{\mathrm{p}}(\mathrm{RM}\cdot)(\mathrm{M}) & (4) \\ \mathrm{RM}_n\cdot + \mathrm{RM}_m\cdot \longrightarrow \mathrm{P} & k_{\mathrm{t}}(\mathrm{RM}\cdot)^2 & (5) \end{array}$$

At the stationary state

$$R_{\mathrm{i}} = k_{\mathrm{t}}(\mathrm{RM}\cdot)^2$$

and the over-all rate is given by the rate of chain propagation

$$R = \frac{-\mathrm{d(M)}}{\mathrm{d}t} = k_{\mathrm{p}}(\mathrm{RM}\cdot)(\mathrm{M}) = \frac{k_{\mathrm{p}}}{k_{\mathrm{t}}^{1/2}}(R_{\mathrm{i}})^{1/2}(\mathrm{M}) \quad (6)$$

If the concentration of monomer is lower than a critical value, some of the primary radicals R· escape scavenging by the monomer and either recombine or react with growing chains. In such event the reaction rate is lower than expected on the basis of equation 6.[17]

The rate of free radical production is equal to the rate of chain initiation R_{i} and can be derived immediately from equation 6

$$R_{\mathrm{i}} = \frac{k_{\mathrm{t}}}{k_{\mathrm{p}}^2} \times \frac{R^2}{(\mathrm{M})^2} \quad (7)$$

It is seen that R_{i} is proportional to the square of the measured over-all polymerization rate.

In order to compare the results of different investigators obtained with a given system under different experimental conditions (temperature and dose rate), it is convenient to consider relative reaction rates with respect to rate of polymerization of the pure monomer R_0. It immediately follows from the equations above that

$$R/R_0 = (R_{\mathrm{i}}/R_{\mathrm{i0}})^{1/2}(\mathrm{M})/(\mathrm{M}_0) \quad (8)$$

and

$$R_{\mathrm{i}}/R_{\mathrm{i0}} = (R/R_0)^2(\mathrm{M}_0)^2/(\mathrm{M})^2 \quad (9)$$

Here R_0, R_{i0} and (M_0) pertain to polymerization in bulk and R, R_{i} and (M) to polymerization in solution.

If free radicals are produced independently from the monomer and from the solvent (*i.e.*, if energy transfer is not operative), the simple additivity rule applies to the system and the over-all rate of initiation is

$$R_{\mathrm{i}} = [\varphi_{\mathrm{M}}(\mathrm{M}) + \varphi_{\mathrm{S}}(\mathrm{S})]I \quad (10)$$

This equation can be modified to

$$R_{\mathrm{i}} = \varphi_{\mathrm{M}}(\mathrm{M})I\left[1 + \frac{\varphi_{\mathrm{S}}}{\varphi_{\mathrm{M}}}\,\frac{(\mathrm{S})}{(\mathrm{M})}\right] \quad (11)$$

φ_{M} can be derived from the rate of polymerization of the pure monomer; hence φ_{S} can be calculated according to equation 11.

In the more general case equation 10 is not applicable and if R_{i} is plotted *versus* (M) a non-linear relationship usually is observed.

It should be noted that when the chemical composition of the mixture is modified while the samples are irradiated in the same radiation field, the absorbed dose can be noticeably different in each set of experiments. It follows that only the exposure dose remains constant in such experiments and

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(8) A. Henglein, C. Schneider and W. Schnabel, *Z. physik. Chem.* **12**, 339 (1957).

(9) (a) P. J. Berry and M. Burton, *J. Chem. Phys.*, **23**, 1969 (1955); (b) P. J. Berry, S. Lipsky and M. Burton, *Trans. Faraday Soc.*, **52**, 311 (1956).

(10) F. H. Brown, M. Furst and H. P. Kallmann, *J. chim. phys.*, **55**, 689 (1958).

(11) A. Chapiro, *ibid.*, **47**, 747, 764 (1950).

(12) Y. Landler, Thesis, University of Paris, 1952.

(13) C. Cousin, Thesis, University of Paris, 1953.

(14) W. H. Seitzer and A. V. Tobolsky, *J. Am. Chem. Soc.*, **77**, 2687 (1955).

(15) A. Chapiro, M. Magat, A. Prevot-Bernas and J. Sebban, *J. chim. phys.*, **52**, 689 (1955).

(16) (a) T. S. Nikitina and Kh. S. Badgasarian, "Sbornik Rabot po Radiazionnoi Khimii," Academy of Sciences USSR, Moscow, 1955, p. 183; (b) S. S. Medvedev, *J. chim. phys.*, **52**, 677 (1955).

(17) A. Chapiro, M. Magat, J. Sebban and P. Wahl, "Internat. Symp. Macromol. chem. Milan-Turin," 1954, Suppl. La Ricerca Scientifica, 1955, p. 73.

hence the symbol I is used to designate exposure dose-rate, expressed in roentgens per second. The reduced rates of free radical production $\varphi_M(M)$ and $\varphi_S(S)$ are expressed in moles of free radicals formed per roentgen per second. G_R values can be derived from the corresponding values of φ according to the equation

$$G_R{}^M = \frac{\varphi_M(M) \times 6.02 \times 10^{23} \times 100}{1000 d_M e_M} \qquad (12)$$

Here d_M is the specific gravity of M and e_M is the amount of energy (in electron volts) absorbed per roentgen in one gram of M. A similar equation applies to values of $G_R{}^S$. In the following, all the G_R values are calculated on the basis of $G(Fe^{3+}) = 15.5$ for the yield of oxidation of ferrous sulfate in 0.8 N sulfuric acid solutions.

III. Experimental Results

Various types of radiations have been used in the past for initiating vinyl polymerizations in solution. These include γ-rays[11,16,18–21] β-particles[14] and mixed radiation from a nuclear reactor.[12,13] Most of the work was carried out with either styrene or methyl methacrylate although a few data are available as well for other monomers. A number of binary mixtures show linear relationships between rates of initiation and chemical composition. These often correspond to compounds having similar chemical structure. Mixtures of other types usually exhibit energy transfer processes.

1. Mixtures Showing a Simple Dilution Effect.—This group of mixtures includes styrene solutions in various aromatic hydrocarbons and methyl methacrylate or vinyl acetate in methyl and ethyl acetate solutions.

A. Styrene Solutions in Aromatic Hydrocarbons.—The radiation polymerization of styrene in benzene, toluene, ethylbenzene and xylene was studied by the author with a 0.4 curie radium source at a single dose rate.[11] Sebban[18] initiated the polymerization of styrene in toluene solutions with cobalt-60 γ-rays over a very broad range of dose rates. The β-ray initiated reaction in both benzene and toluene was reported by Seitzer and Tobolsky.[14] Finally Cousin[13] investigated the polymerization of styrene solutions in benzene in the nuclear reactor Zoé at Chatillon, France.

Linear plots are obtained from most experimental data when plotting the rate of initiation *versus* composition of the mixture. For very dilute solutions, rates are lower than expected, in accordance with the discussion above.[17] In the case of toluene, the agreement reached between all results is excellent and the ratio φ_s/φ_M is found to be 1.5. Assuming a G_R value of 0.69 for pure styrene, which best fits with all experimental data,[22] the G_R value derived for toluene is 1.15. This value is in very close agreement with the G_R value determined for this compound by the DPPH method *in vacuo*, *i.e.*, $G(-DPPH) = 1.1$[23]; it is noticeably lower than the G_R value found with iodine, $G(-I) = 2.36$[24] (see Table I).

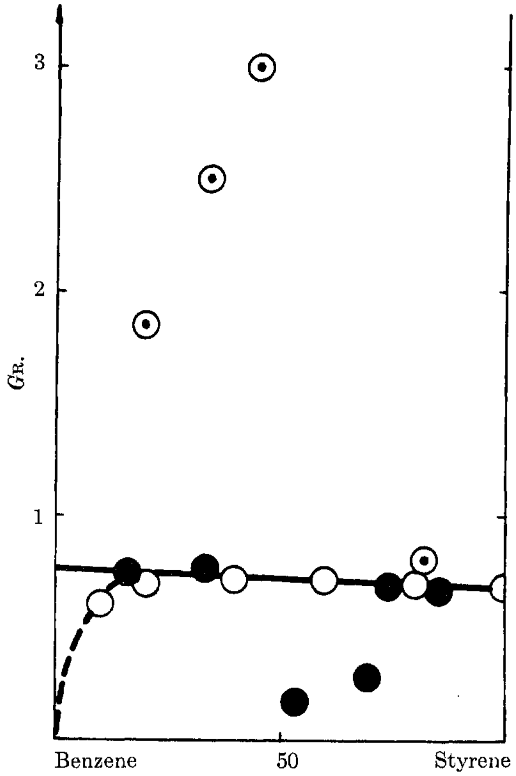

Fig. 1.—Free radical yields in mixtures of styrene with benzene derived from data of the following sources: ○, A. Chapiro[11]; ●, C. Cousin[13]; ⊙, W. H. Seitzer and A. V. Tobolsky.[14]

TABLE I

RELATIVE RATES OF FREE RADICAL PRODUCTION AND G_R VALUES OF AROMATIC HYDROCARBONS DERIVED FROM THE SOLUTION POLYMERIZATION OF STYRENE AND FROM SCAVENGER DATA

Compound	Polymerization			DPPH		Iodine	
	φ_s/φ_m	G_R	Ref.	G_R	Ref.	G_R	Ref.
Styrene	..	0.69	22	0.6	25		
Benzene	0.95	0.74	11	0.6	26	0.66	24
	1.0	0.78	13	0.74	4	0.78[a]	28
	3.1	2.3	14	0.75	25, 27		
Toluene	1.45	1.1	11	1.1	23	2.41	24
	1.55	1.2	14				
Xylene	4.5	2.8	11			2.5	24
Ethylbenzene	6.5	4.0	11			2.8	24

[a] $G(-Fe^{+3})$ determined by the ferric ion method.

In the case of benzene solutions, both the results of Cousin and the earlier results of the author lead to values of φ_S/φ_M very close to unity, whereas the data derived from β-ray experiments are much more scattered and correspond to a higher value. The various results are shown in Fig. 1. The G_R value for benzene derived from the straight line determined by most results is $G_R^{\text{benzene}} = 0.76$. This value agrees well with G_R values for benzene ob-

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(18) J. Sebban, unpublished results; see also references 15 and 17.

(19) K. Hayashi, unpublished results, 1957.

(20) I. Mita, unpublished results, 1957.

(21) P. Cordier, unpublished results, 1957.

(22) A. Chapiro, "Radiation Chemistry of Polymeric Systems," Interscience Publishers, New York, N. Y., to be published. See also A. Chapiro and M. Magat in "Actions chimiques et biologiques des radiations ionisantes," 3ème série, Masson et Cie., Paris, 1958.

(23) N. Gislon, unpublished results, 1957–1958.

(24) E. N. Weber, P. F. Forsith and R. H. Schuler, *Radiation Research*, **3**, 63 (1955).

tained by scavenger studies. The available data on G_R values of aromatic hydrocarbons are summarized in Table I.

B. Methyl Methacrylate Solutions.—The γ-ray initiated polymerization of methyl methacrylate in ethyl acetate solutions was reported by Nikitina and Bagdasarian.[16] These authors found a linear relationship when plotting over-all rates of polymerization *versus* monomer concentration. Such a relationship demonstrates that the simple additivity rule applies to this system and that the over-all rate of free radical production remains constant over the entire range of concentrations. It follows that

$$\varphi_M = \varphi_S$$

and hence that the G_R value of ethyl acetate is close to that of methyl methacrylate. A similar result was found by Sebban[18] for methyl methacrylate solutions in methyl acetate. The rate of polymerization of methyl methacrylate in acetone was reported by Seitzer and Tobolsky.[14] Although the results obtained by these authors are very scattered, a straight line can be drawn through most experimental points when plotting rates of initiation *versus* monomer concentration. The value of φ_S/φ_M derived from these data is 0.72 which leads to a G_R value of acetone in reasonable agreement with results obtained by other methods (see Table II).

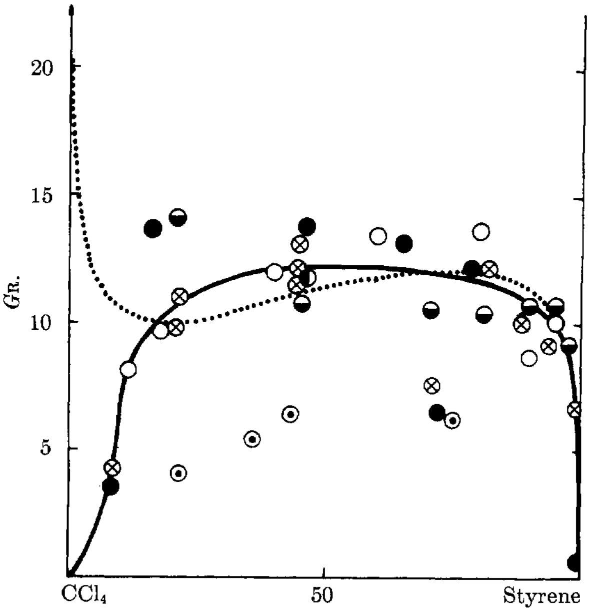

Fig. 2.—Free radical yields in mixtures of styrene with carbon tetrachloride derived from data of the following sources: ○, A. Chapiro[11]; ⊗, Y. Landler[12]; ●, C. Cousin[13]; ⊙, W. H. Seitzer and A. V. Tobolsky[14]; ◒, T. S. Nikitina and Kh. S. Bagdasarian[16]; ◐, P. Cordier.[21] The dotted line is based on G_R-values determined by the DPPH method in mixtures of benzene with carbon tetrachloride.[6]

In order to calculate G_R values from the results above, it is necessary to know the absolute yield of free radical production in the monomer. The G_R value of methyl methacrylate was determined directly by Krongauz and Bagdasarian[25] using the DPPH method. These authors found $G(-\text{DPPH}) = 5.5$ in the pure monomer. This value is roughly two times lower than the G_R value derived from polymerization rate data, *i.e.*, $G_R = 11$–12.[22] The reason for this discrepancy is not known.

It should be noted that the DPPH method *in vacuo* usually leads to lower G_R values than other methods in the case of oxygenated compounds.[29,30] On the other hand G_R values obtained with DPPH in aerated solutions correspond to the higher values.[4]

C. Vinyl Acetate Solutions.—Various mixtures of vinyl acetate and ethyl acetate were irradiated by Nikitina and Bagdasarian[16] in the presence of DPPH. G_R values were not derived from these experiments. It was found however that the rates of disappearance of DPPH were equal in pure vinyl acetate, in pure ethyl acetate and in an equimolecular mixture of these two compounds. It can be concluded from this result that $\varphi_S/\varphi_M = 1$ in this system. The absolute yield of DPPH consumption in ethyl acetate was reported by Krongauz and Bagdasarian to be 7.[27] Here again this value is one-half the G_R value of vinyl acetate derived from kinetic data.[22]

G_R values for these various compounds derived either from polymerization studies or by other methods are listed in Table II.

TABLE II

RELATIVE RATES OF FREE RADICAL PRODUCTION AND G_R VALUES OF OXYGENATED COMPOUNDS DERIVED FROM SOLUTION POLYMERIZATION IN METHYL METHACRYLATE AND VINYL ACETATE AND FROM OTHER METHODS

Compound	Polymerization			DPPH and other methods	
	φ_S/φ_M	G_R	Ref.	G_R	Ref.
Methyl methacrylate	..	11.5	22	5.5	25
Methyl acetate	0.95	10.9	18	6.8	4
				5.5	29
				10.5[a]	30
Ethyl acetate	1	11.5	16	7	27
Acetone	0.72	9.4	14	5.6	29
				11.8	28
Vinyl acetate	..	14	22		
Ethyl acetate	1[b]	14	16	7	27

[a] Derived from an analysis of products of radiolysis. [b] Determined by the DPPH method.

2. Mixtures Exhibiting Energy Transfer.—In the earlier work on radiation-initiated polymerization in solution it was noticed for a number of systems that the ratio φ_S/φ_M did not remain constant but steadily changed with monomer concentration.[11] When the rate of initiation calculated from these data was plotted *versus* monomer concentration, non-linear curves were obtained.[15] A quantitative treatment of these effects was proposed by Nikitina and Bagdasarian[16] on the basis of

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(25) V. A. Krongauz and Kh. S. Bagdasarian, quoted by S. S. Medvedev, Proceedings of the first (UNESCO) International Conference "Radioisotopes in Scientific Research" Pergamon Press, London, 1958, Vol. I, p. 757.

(26) W. Wild, *Faraday Soc. Disc.*, **12**, 127 (1952).

(27) V. A. Krongauz and Kh. S. Bagdasarian, "Deistve ioniziruyushtshikh izluchenii na neorganicheskie i organicheskie sistemy," Academy of Sciences, USSR, 1958, p. 205.

(28) E. A. Cherniak, E. Collinson, F. S. Dainton and G. M. Meaburn, *Proc. Chem. Soc.*, 54 (1958). See also R. A. Back, *et al.*, Second United Nations International Conference on the Peaceful Uses of Atomic Energy, Geneva 1958, 15/P/1516.

(29) W. Wild, *J. chim. phys.*, **52**, 653 (1955).

(30) P. Ausloos and C. Trumbore, to be published.

an energy transfer process. A similar scheme was developed further by Bouby.[5,6] In the following, several monomer-solvent mixtures are considered in which these effects are particularly pronounced.

A. Styrene Solutions in Carbon Tetrachloride.—Radiation polymerization of styrene solutions in carbon tetrachloride was studied by a number of investigators using γ-rays,[11,16,21] β-particles[14] and mixed radiation from a nuclear reactor.[12,13] In order to compare these various results, the rate of radiation polymerization of pure styrene was used as a chemical dosimeter. Relative rates of polymerization in solution with respect to the reaction in bulk were calculated from experimental data and from these the relative rates of initiation were derived (see equation 8). G_R values for the mixtures are plotted in Fig. 2. The experimental points show considerable scatter partly because G_R values are proportional to the square of measured polymerization rates. Average deviations from the solid line are of the order of 20%. The general agreement between results obtained with γ-rays and reactor radiation is satisfactory, whereas β-ray experiments definitely show a different trend. The reason for this discrepancy is not clear. It can be seen that the addition of small amounts of carbon tetrachloride to styrene leads to a very important sensitization of the reaction. A similar effect was observed in mixtures of benzene with carbon tetrachloride. The dotted line in Fig. 2 shows G_R values obtained by the DPPH method for carbon tetrachloride benzene mixtures *in vacuo*.[6] When comparing the two curves it appears that the results are almost identical for both systems over most of the range of concentrations studied. However, in solutions containing more than 80% carbon tetrachloride, the two curves are distinctly separated. In this range of concentrations, benzene strongly "protects" carbon tetrachloride, as shown by the experiments with DPPH, whereas in styrene solutions this effect, if it does take place, is hidden by a sudden drop in rate of initiation owing to incomplete scavenging of primary radicals by the monomer.

It is of interest that Bagdasarian[31] obtained an identical relationship between over-all rate of polymerization and monomer concentration when using either γ-rays or ultraviolet light for initiating the reaction. This observation demonstrates that the processes occurring in this reaction involve only transfer of excitation energy and that transfer of charge is unimportant. On the other hand, the good agreement reached between the results of the various investigators who worked at different reaction temperatures (between 15 and 40°) and with both γ-rays and mixed radiation from the nuclear reactor, demonstrates that these excitation transfer processes only depend to a small extent on temperature and on type of radiation.

B. Styrene Solutions in Chloroform.—The results obtained with styrene solutions in chloroform are very similar to those found in carbon tetrachloride. The former mixture was studied using γ-rays,[11] β-particles[14] and reactor radiation.[13] The results are shown in Fig. 3. Here again the polymerization data show a similar trend to the data obtained by the DPPH method for chloroform–benzene mixtures.[4,6] This is shown by the dotted curve. In both systems the addition of small

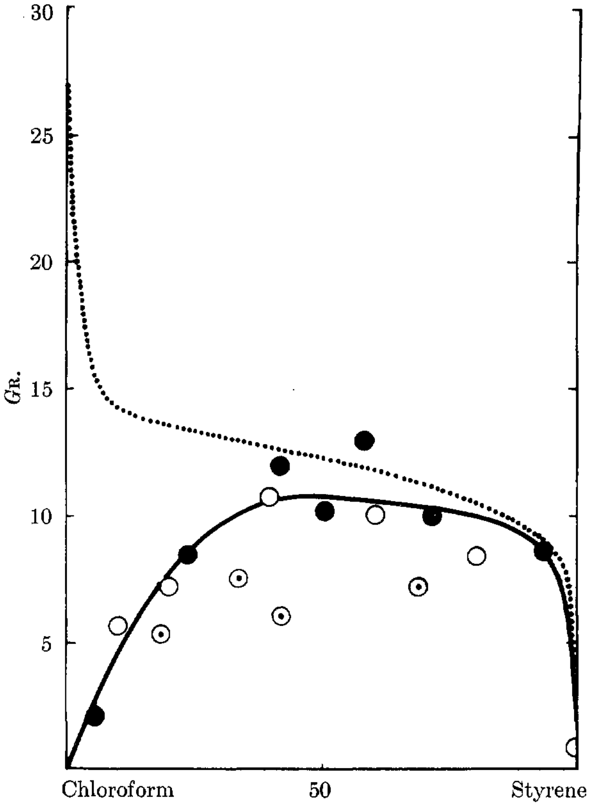

Fig. 3.—Free radical yields in mixtures of styrene with chloroform derived from data of the following sources: ○, A. Chapiro[11]; ●, C. Cousin[13]; ⊙, W. H. Seitzer and A. V. Tobolsky.[14] The dotted line is based on G_R-values determined by the DPPH method in mixtures of benzene with chloroform.[4,4]

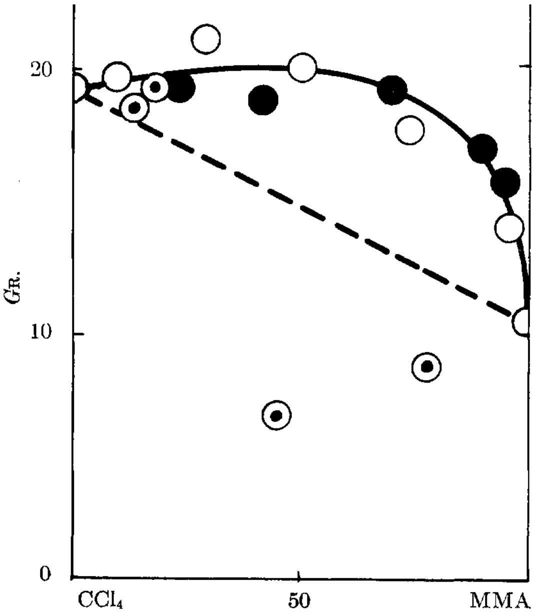

Fig. 4.—Free radical yields in mixtures of methyl methacrylate with carbon tetrachloride derived from data of the following sources: ⊙, W. H. Seitzer and A. V. Tobolsky[19]; ●, T. S. Nikitina and Kh. S. Bagdasarian[16]; ○, K. Hayashi.[14]

[31] Kh. S. Bagdasarian, Thesis, Institut Karpov Moscow, 1950. See also ref. 16b and 25.

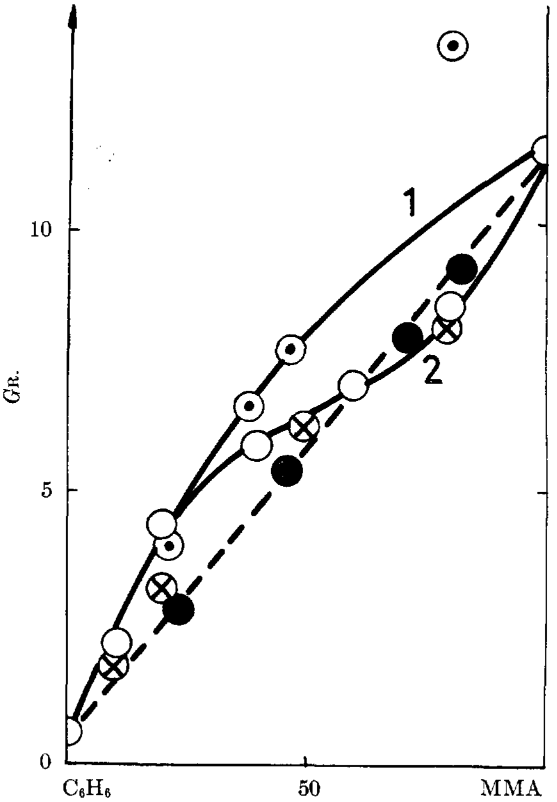

Fig. 5.—Free radical yields in mixtures of methyl methacrylate with benzene derived from data of the following sources: ○, A. Chapiro[11]; ⊙, W. H. Seitzer and A. V. Tobolsky[14]; ●, T. S. Nikitina and Kh. S. Bagdasarian[16]; ⊗, I. Mita.[20]

amounts of chloroform to the aromatic hydrocarbon leads to a strong sensitization. The deviation occurs at lower concentrations of monomer than in carbon tetrachloride solutions. In addition the dotted curve shows that small amounts of benzene very efficiently "protect" chloroform.

C. Methyl Methacrylate Solutions in Carbon Tetrachloride.—Carbon tetrachloride strongly sensitizes the polymerization of methyl methacrylate. The reaction was initiated both with γ-rays[16,19] and with β-particles[14]; the latter results are very scattered. G_R values for this system are plotted in Fig. 4 using the higher G_R value for methyl methacrylate, *i.e.*, $G_R^{MMA} = 11.5$[22] The G_R value thus obtained for pure carbon tetrachloride is 19, a value which is reasonably close to the result obtained by the DPPH method *in vacuo*, *i.e.*, $G_R^{CCl_4} = 18$–20.[5,6,23] It should further be noticed that even in very dilute solutions the monomer acts as a very efficient free radical scavenger in this system.

The curve in Fig. 4 shows a flat maximum at approximately 80% CCl_4. A very similar curve was obtained when plotting G_R values for mixtures of chloroform and methyl acetate determined by the DPPH method.[4] Here again the agreement reached by the two methods is very good.

D. Methyl Methacrylate Solutions in Benzene.—The radiation initiated polymerization of methyl methacrylate in benzene solution proceeds at a lower rate than in bulk over the entire range of concentrations. This reaction was studied with γ-rays[11,16,20] and with β-particles.[14] Figure 5 shows a plot of G_R values derived from all available data. It should be noted that the accuracy in deriving rates of initiation from polymerization data is very poor when G_R^S is lower than $G_R^{M'}$; *i.e.*, when $\varphi_S/\varphi_M < 1$. It follows that it is difficult to conclude definitely from the data whether energy transfer actually takes place in this system or not. It can be seen from the plot in Fig. 5 that the data of Nikitina and Bagdasarian[15] lead to an almost linear relationship between G_R and concentration; the data of Seitzer and Tobolsky[14] are consistent with a sensitizing effect (curve 1), whereas the earlier data of the author[11] as well as the more recent experiments of Mita[20] indicate sensitization for low monomer concentrations and "protection" in concentrated monomer solutions (curve 2). It is noteworthy that a curve of type 1 was obtained for free radical yields in mixtures of benzene with methyl acetate by the DPPH method *in vacuo* whereas a curve of type 2 was found in aerated solutions.[32]

E. Other Systems.—A number of data are available on radiation-initiated solution polymerization of several other systems. The results are usually too scattered or involve too complicated processes to make it possible to derive any quantitative information on radical yields of the added substance. In a few special cases however more systematic work has been carried out. A brief survey of the data is presented below.

(a) **Styrene Solutions.**—Butylamine, dibutylamine, benzylamine and aniline all significantly sensitize the γ-ray initiated polymerization of styrene.[11] The effect is less pronounced with aniline than with aliphatic amines. The experimental data do not fit with the simple energy transfer theory developed by Nikitina and Bagdasarian.[16] This situation presumably results from the fact that amines inhibit vinyl polymerization. The results obtained by adding small amounts of amine to the monomer suggest that energy transfer takes place in the radiolysis of these mixtures leading to very strong sensitization. Quantitative data on the influence of amines on polymerization rates are still scarce and the mechanism of this inhibition is not definitely established. Hence G_R values for amines cannot be derived from these data.

Inhibition seems to be operative as well when ethyl iodide[14] and carbon disulfide[11] are added to styrene. The radiolysis of these substances leads to the formation of iodine and sulfur, respectively; the latter are known to act as efficient polymerization inhibitors. It is interesting to notice that protection is observed when carbon disulfide is dissolved in chloroform whereas some sensitization occurs in carbon disulfide–benzene mixtures.[5]

Diphenylmethane, unlike other aromatic hydrocarbons, strongly sensitizes the radiation polymerization of styrene; the same applies to the addition of small amounts of hydroquinone to styrene.[33]

Benzoyl peroxide produces an important increase in the rate of styrene polymerization,[33]

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(32) L. Bouby and A. Chapiro, *J. chim. phys.*, **54**, 341 (1957).

(33) A. Chapiro, unpublished results.

whereas *t*-butyl peroxide does not show any pronounced effect.[14] This observation can be interpreted on the basis of more recent work on the radiolysis of peroxide solutions in various solvents. Thus Krongauz and Bagdasarian found that when benzoyl peroxide was irradiated in benzene solution a very rapid decomposition ensued which led to an apparent $G(-Bz_2O_2)$ of the order of 1700.[27] It was demonstrated that the reaction did not proceed through a chain mechanism and hence a very efficient energy transfer process was assumed to occur in this system. No energy transfer was observed in cyclohexane and ethyl acetate solutions but the decomposition of benzoyl peroxide occurred through a chain reaction in these two solvents. The addition of small amounts of methyl methacrylate prevented chain propagation and reduced the over-all $G(-Bz_2O_2)$. On the other hand, *t*-butyl peroxide, when dissolved in either benzene, cyclohexane or methyl acetate, decomposed exclusively by a straightforward reaction apparently without energy transfer. The observed G-value was $G(\text{-peroxide}) = 17$.[34] The G_R value for decomposition of benzoyl peroxide was found to be 40.[27] If one assumes that the behavior of these peroxides is similar in styrene and in benzene solutions, it becomes clear why only benzoyl peroxide sensitizes the radiation polymerization of styrene.

Experiments were carried out as well with solutions of styrene in ether,[11] nitrobenzene, propionitrile,[33] bromoform[12] and dioxane.[14] In all cases the reaction rate increased with dilution.

Protection seemed to be operative in styrene solutions in cyclohexane and in *n*-heptane. In contrast, strong sensitization occurred in various alcohols and in acetone.[11] In these mixtures, however, polymer precipitation during the reaction leads to anomalous kinetic behavior.

The radiation polymerization of styrene dissolved in binary mixtures of carbon tetrachloride and benzene also was investigated.[14] The rate was found to be higher in the mixtures than in either solvent alone.

(b) **Methyl Methacrylate Solutions.**—Only little information is available on the influence of other additives on the radiation polymerization of methyl methacrylate. Experiments were carried out by Seitzer and Tobolsky[14] with ethyl bromide, ethyl iodide and dioxane. The results indicate a sensitizing effect in most cases. Methyl methacrylate dissolved in binary mixtures of carbon tetrachloride and benzene was found to polymerize faster than in carbon tetrachloride alone. On the other hand, the addition of water to methyl methacrylate solutions in dioxane increased the polymerization rate whereas water had no significant effect on the rate of polymerization in acetone solutions. The higher rates observed in dioxane–water mixtures were assumed to arise as a result of the tighter coiling of growing chains in the poor solvent which would be expected to slow down the termination step.

(c) **Vinyl Acetate Solutions.**—The radiation polymerization of vinyl acetate was found to be strongly inhibited by the addition of small amounts of benzene.[16] It is difficult to draw any conclusion on the existence of energy transfer from this result since benzene is known to inhibit polymerization of vinyl acetate when initiated by conventional means, presumably by a deactivating copolymerization mechanism.[35] A few experiments were conducted with diphenylpicrylhydrazyl in mixtures of vinyl acetate and benzene.[16] The rate of disappearance of DPPH indicated that sensitization takes place in a similar manner as in mixtures of benzene with methyl methacrylate and methyl acetate. On the other hand, carbon tetrachloride, which strongly sensitizes radiation polymerization of both styrene and methyl methacrylate, does not produce any measurable increase in the polymerization rate of vinyl acetate.[16]

IV. General Conclusions

The various data presented herein show how radiation polymerization can be applied to the study of the radiolysis of binary mixtures. The advantages of this method are primarily that conventional analytical techniques can be used for determining primary yields and that no foreign compound is added to the system since one of the two components acts as a scavenger. On the other hand, the method is necessarily limited to mixtures in which the polymerization kinetics are not complicated by secondary effects such as polymer precipitation, inhibition, etc. Furthermore, the rate constants of chain propagation and termination must be accurately known for the monomer used. Finally it should be stressed that since the reaction rate measured experimentally is proportional to the square root of free radical yield, this method is generally less sensitive than the direct determination of free radicals by other scavenger methods.

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[34] V. A. Krongauz and Kh. S. Bagdasarian, *Zh. fiz. Khim. U.S.S.R.*, **32**, 717 (1958).

[35] W. H. Stockmayer and L. H. Peebles, *J. Am. Chem. Soc.*, **75**, 2279 (1953).