the partially oxidized inhibitor. The visible absorption spectrum of one such solution was measured and the characteristic absorption maxima at 565 and 615 mμ were used to estimate the concentration of the ion. The intensity of the absorption was about 5% of what it would have been if all of the inhibitor were present as the Würster cation. Identical observations were made in an experiment in which water was added before the reaction was started. Blank experiments were run without initiator to determine that the formation of the Würster cation was not due to air oxidation. The cation was formed but only to a barely perceptible extent during the time involved in these experiments.

Acknowledgment.—We are very grateful for the generous support of this study by the B. F. Goodrich Co.

AMES, IOWA

[A CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

The Efficiency of Radical Production from Azo-bis-isobutyronitrile

BY GEORGE S. HAMMOND, JYOTIRINDRA N. SEN AND CHARLES E. BOOZER

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Radicals are produced in pairs by the thermal decomposition of azo-bis-isobutyronitrile (AIBN). It is shown that an appreciable fraction of these radicals react with each other before they diffuse apart. The evidence consists of the demonstration that various radical scavengers such as butyl mercaptan, α,α-diphenyl-β-picrylhydrazyl (DPPH), iodine and oxygen do not capture the decomposition products quantitatively. Quantitative efficiency measurements have been carried out with the last three scavengers. It is shown that DPPH does not give an accurate count of the radicals produced but leads to variable underestimation of the rate of radical production. However, efficiencies measured by iodine scavenging and by a method involving the use of oxidation inhibitors give quantitative agreement in five different solvents.

There are various indications that the efficiency of production of free radicals in thermal decomposition reactions may not reach 100%. Arnett and Peterson[1] have reported that the efficiency of initiation of styrene polymerization by AIBN is only about 60% and that the efficiency of initiation of other monomers by the same initiator varies upward from this figure reaching 100% with acrylonitrile. Bateman and Morris[2] found evidence that the initiation of oxidation of butyl acetate, tetralin and digeranyl by AIBN and benzoyl peroxide was measurably inefficient. Inefficiency in radical production from benzoyl peroxide has been observed frequently but is, at least in part, interpretable as being due to the wastage of the initiator by chain decomposition.[3] However, it has been shown repeatedly that the decomposition of azonitriles is free of such complications.[4,5] A reasonable explanation of the inefficiency is found in the observation that the recombination and disproportionation of the radicals produced from the initiator may be diffusion controlled reactions. If this is the case some of the radical pairs produced in the primary decomposition process may destroy each other before they diffuse apart. It has previously been suggested on the basis of a study of the fate of benzoyloxy radicals produced in the decomposition of benzoyl peroxide that such "cage effects" may account for some of the anomalous behavior exhibited by these radicals.[6]

It was the purpose of the present study to carry out a careful investigation of the efficiency of radical production from AIBN by carrying out the decomposition in the presence of efficient radical scavengers. Efficiencies can be studied either by comparing the rate of disappearance of the scavenger with the rate of decomposition of AIBN or by studying the products formed from the azo compound.

Experimental

Azo-bis-isobutyronitrile was recrystallized twice from aqueous alcohol. The substance melted at 102° with decomposition. Infrared spectra as well as nitrogen evolution experiments showed the absence of tetramethylsuccinonitrile.

n-Butyl Mercaptan.—Eastman Kodak white label material was dried over Drierite and fractionated twice in nitrogen atmosphere. The concentrations of mercaptan in each of the mixtures were determined accurately by the iodine method.[7]

α,α-Diphenyl-β-picrylhydrazyl was prepared by the method of Goldschmidt and Renn,[8] and was purified by recrystallizing from chloroform (m.p. 140°). Solutions of DPPH in the various solvents used showed an absorption maximum at 5200 Å. and obeyed Beer's law throughout and beyond the range of concentrations used in the present work.

Baker and Adamson reagent quality resublimed iodine was used. Solutions of iodine in carbon tetrachloride, benzene, toluene, chlorobenzene and nitromethane showed absorption maximum at 5200, 5000, 5100 and 4800 Å., respectively. Optical density measurement in the various solvents were carried out at the respective wave length of maximum absorption as cited above. A slit width of 0.02 mm. has been used in every case.

Solvents.—Toluene, carbon tetrachloride, chlorobenzene, nitromethane and benzene were purified, dried and fractionated by usual methods.

Studies with n-Butyl Mercaptan.—AIBN (8.20 g., 0.05 mole) was dissolved in 250 ml. of solvent containing known amounts of n-butyl mercaptan. The mixture, contained in a liter flask, was frozen in a Dry Ice-acetone-bath, evacuated and sealed under vacuum. The sealed flask was immersed in an oil-bath maintained at 80 ± 0.1°. Reaction was allowed to take place for about 20 hours which equals 16 half-life periods for the decomposition of AIBN at 80°. The flask was cooled, opened, and the solvent and mercaptan were removed by evaporation under reduced pressure at room temperature. The residue, usually a mixture of yellowish oil and white crystals, was filtered carefully,

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(1) L. M. Arnett and J. H. Peterson, THIS JOURNAL, **74**, 2031 (1952); L. M. Arnett, *ibid.*, **74**, 2027 (1952).

(2) L. Bateman and A. L. Morris, *Trans. Faraday Soc.*, **48**, 1149 (1952).

(3) K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946); **69**, 2299 (1947).

(4) F. M. Lewis and M. S. Matheson, *ibid.*, **71**, 747 (1949).

(5) C. G. Overberger, M. T. O'Shaughnessy and H. Shalit, *ibid.*, **71**, 2661 (1949).

(6) G. S. Hammond, J. T. Rudesil and F. J. Modic, *ibid.* **73**, 3929 (1951).

(7) Sidney Siggia, "Quantitative Analysis *via* Functional Groups," John Wiley and Sons, Inc., New York, N. Y., 1949, pp. 85–86.

(8) S. Goldschmidt and K. Renn, *Ber.*, **55**, 628 (1922).

washed with cold aqueous alcohol and the recovered solid was mixed with the first crop. The whole lot was then recrystallized from aqueous alcohol, filtered, dried and weighed. The product, tetramethylsuccinonitrile, melted at 167–168°. Two control experiments in each of the two solvents, carbon tetrachloride and toluene, in absence of mercaptan gave reproducible yields of tetramethylsuccinonitrile (86.8% in toluene and 96.2% in carbon tetrachloride). Various experiments were run under comparable conditions to establish that neither the solvent nor the dinitrile formed are involved in any reaction with the mercaptan.

Studies with DPPH.—(A) Calculated volumes of DPPH and AIBN solutions were pipetted into the reaction vessel which was provided with a nitrogen bubbling device, a standard taper joint for withdrawing samples and a condenser. This was diluted with a known volume of the solvent to bring the optical density of the resultant solution to a conveniently and accurately measurable value. The concentration of AIBN used in all these experiments has been at least ten times greater than the concentration of DPPH. Nitrogen gas was bubbled through the solution for a period of about ten minutes to remove the dissolved oxygen from the solution. The reaction then was started by immersing the reaction vessel in an oil-bath maintained at 62.5°. Throughout the whole experiment the system was kept under a slight positive pressure of nitrogen. Samples were pipetted out at different intervals into glass-stoppered 10-ml. flasks cooled in an ice-bath. Optical densities of the different samples were measured in a model DU Beckman spectrophotometer. The time for complete reaction (t_c) was determined by the method of Bawn and Mellish.[15]

(B) **Sealed Tube Experiments.**—The reaction mixture, as before, was saturated with nitrogen and 8-ml. portions of this solution were pipetted into scrupulously cleaned test-tubes. The contents were frozen, evacuated, flushed with nitrogen and allowed to melt. The process of freezing, evacuation and flushing with nitrogen was repeated three times and the tubes were finally sealed under solvent vapor at a reduced pressure. The samples were heated at 62.5° for varying time intervals after which the ampoules were opened and the contents were analyzed for DPPH by the spectrophotometric method.

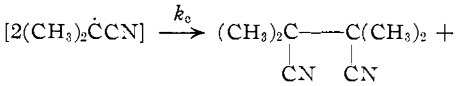
Studies with Iodine.—The same procedure as was described in the case of sealed tube experiments with DPPH was adopted in this work.

Studies with Inhibitors in Oxidation of Olefins.—The details of the experimental procedure and the results of this method are reported in a separate paper.[9] It has been observed that the rate of disappearance of the inhibitor is independent of its concentration. From a determination of the inhibition period produced by a known amount of inhibitor at a known inhibitor concentration, it is possible to estimate the apparent decomposition rate and hence the efficiency factor of the initiator. The work was done with different inhibitors in various substrates with AIBN as the initiator at 62.5°.

Results and Discussion

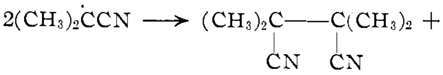
The decomposition of AIBN may be represented by the following equations in which brackets are used to indicate pairs of radicals which have not been separated by diffusion.

$$\mathrm{AIBN} \xrightarrow{k_i} [2(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{CN}] + \mathrm{N_2} \qquad (1)$$



$$[2(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{CN}] \xrightarrow{k_c} (\mathrm{CH_3})_2\underset{\mathrm{CN}}{\mathrm{C}}\text{——}\underset{\mathrm{CN}}{\mathrm{C}}(\mathrm{CH_3})_2 + \text{disproportionation products} \qquad (2)$$

$$[2(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{CN}] \xrightarrow{k_d} 2(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{CN} \qquad (3)$$



$$2(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{CN} \longrightarrow (\mathrm{CH_3})_2\underset{\mathrm{CN}}{\mathrm{C}}\text{——}\underset{\mathrm{CN}}{\mathrm{C}}(\mathrm{CH_3})_2 + \text{disproportionation products} \qquad (4)$$

By careful operation it was possible to isolate yields of 87 and 96% of tetramethylsuccinonitrile from the mixtures produced by the decomposition of AIBN in toluene and in carbon tetrachloride at 80°. This result is in agreement with that of Bickel and Waters[10] who found that high yields of the dinitrile are produced by the decomposition of the azonitrile in toluene at a higher temperature. They also reported the identification of disproportionation products so it seems probable that a material balance, if completed, would not involve any products derived from either of the solvents. The addition of *n*-butyl mercaptan to the decomposition mixture in either solvent leads to a marked decrease in the yield of dinitrile. This indicates the occurrence of reaction 5 which would be expected on the basis of the report by Kooyman[11] and the familiar fact that mercaptans are excellent chain transfer agents in vinyl polymerization.[12] Reduction of the yield of dinitrile may also be due to the reaction of thiyl radicals with cyanoalkyl radicals and attack on the solvent by the sulfur radicals probably occurs. However, the key to all of these reactions is reaction 5 so that the yield of dinitrile may be taken as a semi-quantitative indication of the importance of that reaction. As is shown in Fig. 1 the yields of dinitrile fall with increasing mercaptan concentration, but in both solvents the limiting yield at very high mercaptan concentration is not zero. Since at these concentrations the yield has become independent of the mercaptan concentration the rate of reaction 5 must have become zero order with respect to the mercaptan concentration. This would mean that all of the radicals which are being scavenged are swept from the solution by the mercaptan. It seems an unescapable conclusion that *there must be two reactions which produce the dinitrile,* one which is subject to scavenging by the mercaptan and one which is not. A logical explanation is found in the view

$$(\mathrm{CH_3})_2\dot{\mathrm{C}}\mathrm{CN} + \mathrm{RSH} \longrightarrow (\mathrm{CH_3})_2\mathrm{CHCN} + \mathrm{RS}\cdot \qquad (5)$$

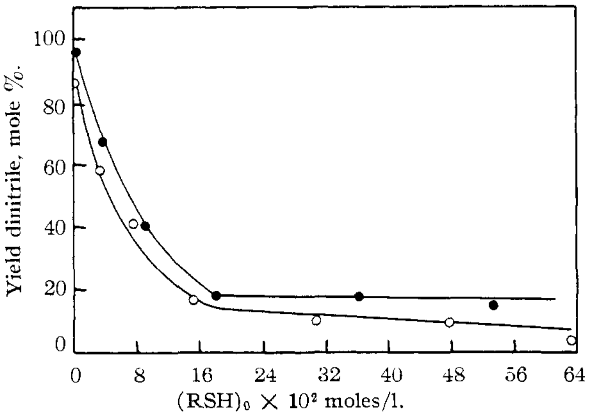


Fig. 1.—Yield of tetramethylsuccinonitrile produced by decomposition of AIBN in the presence of varying amounts of *n*-butyl mercaptan; [AIBN] = 0.2 *M;* ○, in toluene; ●, in carbon tetrachloride.

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[9] C. E. Boozer, G. S. Hammond, C. E. Hamilton and J. N. Sen, THIS JOURNAL, **75**, 3233 (1955).

[10] A. F. Bickel and W. A. Waters, *Rec. trav. chim.*, **69**, 312 (1950).

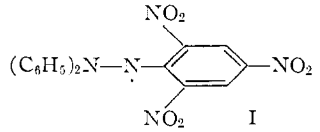
[11] P. Bruin, A. F. Bickel and E. C. Kooyman, *ibid.*, **71**, 1115 (1952).

[12] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 147.

that reaction 5 is fast enough to be competitive with reaction 4 but not with reactions 2 and 3, the diffusion-controlled reactions.

We would not maintain any hope for the quantitative nature of the results at high mercaptan concentrations. The isolated yields of dinitrile are completely reproducible under any given set of conditions, but it is entirely possible that the crystallization of the product leaves increasingly large amounts in the mother liquor as the total yield of non-volatile, sulfur-containing products is increased. Our other studies seem to imply that this is probably the case. However, the indication that reaction 2 is more important in carbon tetrachloride than toluene is in agreement with our other observations.

In attempting to carry out quantitative studies of the "cage effect" it was deemed desirable to use scavengers which are even more efficient than mercaptans in order to enable us to work with relatively low concentrations of the scavenger and measure accurately the changes in concentration of scavenger. It has been reported by a number of workers that α,α-diphenyl-β-picrylhydrazyl (I = DPPH) is a very reactive interceptor of free radicals.[13-15] It is always found that it completely inhibits vinyl polymerizations and disappears at a rate which is zero order with respect to its concentration. This is to be expected if reaction 6 occurs with very high efficiency.


I

$$R\cdot + \text{DPPH} \longrightarrow \text{stable products} \qquad (6)$$

Pursuant to these observations Bawn and Mellish[12] have suggested the use of DPPH in the measurement of the slow rates of decomposition of initiators at low temperatures. The inclusion of reaction 6 in the AIBN decomposition scheme leads to equation 7 if it is assumed that reaction 4 becomes unimportant.

$$d[\text{DPPH}]/dt = 2ak_i[\text{AIBN}] \qquad (7)$$

$$a = k_d/(k_c + k_d) \qquad (8)$$

The application of this equation to the determination of k_1 is subject to two assumptions. The first is that a is actually one, that is, that no recombination of primary radical pairs occurs. The second is that the stoichiometry of radical destruction is as implied by equations 6. We noticed, as has Walling,[16] that the rates of decomposition of AIBN estimated by equation 7 do not agree very well with those calculated by extrapolation of the rates measured at higher temperatures by nitrogen evolution. We were inclined to attribute the discrepancy to the failure of the first assumption and therefore undertook a program designed to measure a by the direct comparison of the rates of disappearance of DPPH with the rates of nitrogen evolution measured at the same temperatures. The values of ak_i were found to be in excellent agreement with those calculated by Bawn and Mellish and were substantially lower than the values of k_1 determined by nitrogen evolution at the same temperature, when the experiments were conducted by heating the solutions from which oxygen had been removed by superficial flushing with nitrogen. The results, which are summarized in Table I, were highly reproducible and the values of a were independent of the concentrations of both AIBN and DPPH in carbon tetrachloride, benzene and chlorobenzene. Measurements made in toluene showed that a varied with the concentration of DPPH and that at relatively high concentrations a actually exceeded one. Since it was also found that solutions of DPPH in toluene faded slowly at the temperature chosen for measurement the data for toluene solution were rejected.

TABLE I

EFFICIENCY FACTORS DETERMINED BY DPPH LIFETIME MEASUREMENT AT 62.5°

Solvent	[DPPH] $\times 10^3$, mole/l.	[AIBN] $\times 10^2$, mole/l.	t_c, min.	a[a]
Carbon tetrachloride	0.124	0.656	34	0.39
	.0773	.492	31.5	.35
	.124	.656	51	.26[b]
	.0773	.492	43.5	.26[b]
Benzene	.112	.312	21	1.00
	.112	.325	21	0.99
	.112	.190	35	.98
	.112	.190	67	.51[b]
	.112	.190	67	.51[b]
	.127	.340	45.5	.48[b]
Chlorobenzene	.0717	.259	23.5	.64
	.143	.680	27	.42[b]
	.133	.615	27.5	.43[b]
	.133	.615	27.5	.43[b]
	.133	.246	67.5	.43[b]

[a] Values of k_i determined by the rate of nitrogen evolution at 62.5° in different solvents are: carbon tetrachloride, 11.8×10^{-6} sec.$^{-1}$; benzene 14.2×10^{-6} sec.$^{-1}$; chlorobenzene 15.4×10^{-6} sec.$^{-1}$. [b] Sealed tube experiments.

Inspection of the a values obtained by the DPPH method reveals one alarming fact. The values for carbon tetrachloride solution are lower than those for the aromatic solvents which is not surprising in view of our mercaptan study. Furthermore, the values obtained for carbon tetrachloride solution were in approximate agreement with those obtained by the antioxidant method described below. This agreement was only fair for chlorobenzene solution and disappeared completely for benzene solution. Since the other method indicated that efficiencies were essentially the same in benzene and chlorobenzene we were led to believe that the DPPH method might be suspected and that the scavenger might be demonstrating a variable stoichiometry in the apprehension of free radicals. Since it has been observed[17] that traces of oxygen interfere with the clean functioning of DPPH we carried out experiments in which all traces of oxygen were removed by exhaustive degassing of individual samples. Application of the procedure again gave re-

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(13) P. D. Bartlett and H. Kwart, THIS JOURNAL, **72**, 1051 (1950).

(14) M. S. Matheson, E. E. Auer, E. B. Bevilacqua and E. J. Hart, *ibid.*, **73**, 1700 (1951).

(15) C. E. Bawn and S. F. Mellish, *Trans. Faraday Soc.*, **47**, 1216 (1951).

(16) C. Walling, *J. Polymer Sci.*, **14**, 214 (1954).

(17) P. D. Bartlett and J. Kice, private communication.

producible values for the efficiency factor, *a*, which were, however, all lower than the values obtained by the previous procedure. Furthermore, the efficiencies measured by this method were all lower than those obtained by the antioxidant method. An additional qualitative observation casts more light on these perplexing phenomena. A chlorobenzene solution which had been degassed and heated *in vacuo* until the picrylhydrazyl color had entirely disappeared was opened and allowed to stand in contact with the atmosphere for several hours. During this time the color of DPPH reappeared indicating that some species was produced which was susceptible to easy air oxidation. This was apparently not diphenylpicrylhydrazine since the latter was not oxidized at a comparable rate when added to solutions in which decompositions had been carried out. The exact nature of these changes is not understood but it is apparent that the reaction of DPPH with radicals must involve at least two different paths, one which gives stable products and the other to give a substance, probably a disproportionation product, which can regenerate DPPH either by reaction with oxygen or by reaction with free radicals. In the absence of oxygen a partial regeneration process probably occurs as, for example by reactions 9 and 10.

$$(CH_3)_2\underset{\cdot}{C}CN + DPPH \longrightarrow CH_2{=}C(CH_3)CN + H{-}DPPH \quad (9)$$

$$H{-}DPPH + (CH_3)_2\underset{\cdot}{C}CN \longrightarrow (CH_3)_2CHCN + DPPH \quad (10)$$

In the presence of traces of oxygen reaction 10 may be replaced by an oxidative reaction involving oxygen but other reactions must also occur to account for the fact that DPPH disappears at a rate which is faster than would be predicted on the basis of the *a* values determined in other ways.

The only conclusion to be drawn from this particular phase of the study is that the use of DPPH for counting radicals is not to be recommended. This is especially true in view of the deceptive reproducibility which was encountered in this work when oxygen was removed from the system by a superficial procedure. It is also proper to point out that too much confidence has probably been placed upon the tacit assumption that radicals react with DPPH by an uncomplicated addition reaction to give stable products. Certainly there is an excellent possibility that disproportionation to give diphenylpicrylhydrazine or other labile products may occur.

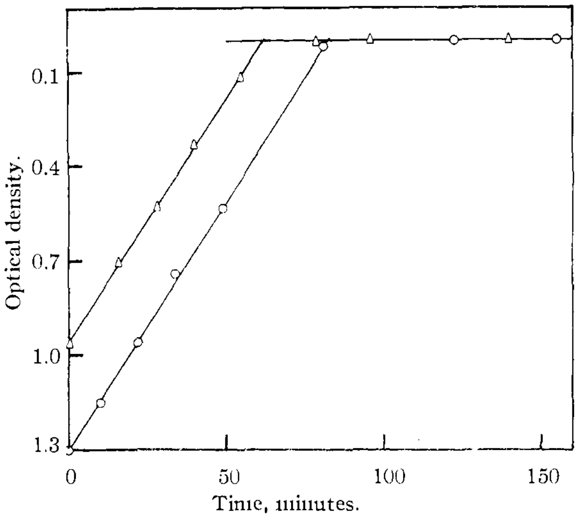

Fig. 2.—Rate of disappearance of iodine in carbon tetrachloride solution containing 4.89 × 10^{-2} *M* AIBN at 62.5°: △, $[I_2]_0$, 1.00 × 10^{-3} *M*; ○, $[I_2]_0$, 1.34 × 10^{-3} *M*.

Because of the failure of DPPH to give reliable results we turned to iodine, another reactive radical scavenger. Since it can be determined spectrophotometrically, it can be used in dilute solutions in the same way as DPPH. It was observed that if solutions containing iodine and an excess of AIBN were heated, the iodine disappeared at a zero-order rate which could be extrapolated, as shown by Fig. 2, to give zero-order lifetimes which were proportional to the initial iodine concentrations. Applications of equation 7 to the results gave the values of *a* listed in Table II. It was observed, furthermore that if solutions containing AIBN and excess iodine were heated until nearly all of the azonitrile had been decomposed, the amount of iodine destroyed was that expected on the basis of the same values of *a*. This latter type of experiment did not give reproducible results in very dilute solutions for reasons which have not yet been discovered. The method does, however, seem to have much to recommend it for counting and trapping radicals, at least in this system. In general the use of iodine as a radical trap should give reliable stoichiometry if the products of iodination are stable. That this is not the case has been shown in scavenging experiments in the decomposition of benzoyl peroxide.[18] In this particular study the product is certainly the α-iodonitrile[19] which does undergo decomposition if it is worked up. There is good evidence that decomposition does not occur under the conditions

TABLE II

EFFICIENCY FACTOR DETERMINED BY IODINE LIFETIME MEASUREMENT AND OXIDATION INHIBITION METHOD AT 62.5°

Solvent	[Iodine] × 10^3, moles/l.	[AIBN] × 10^2, moles/l.	t_0, min.	a^a
Carbon tetrachloride	1.002	2.91	112	0.43
	1.336	4.89	83	.46
	1.002	4.89	62.5	.46
	Oxidation inhibition			.43
Benzene	0.935	4.34	40.5	.62
	Oxidation inhibition			.61
Chlorobenzene	0.894	4.46	36.5	.59
	1.025	4.39	42	.60
	Oxidation inhibition			.57
Nitrobenzene	2.06	6.51	39	.75
	Oxidation inhibition			.73
Nitromethane	0.623	2.82	37	.74
	1.582	5.55	47.5	.75
	Oxidation inhibition			.73

[a] Values of k_i determined by the rate of nitrogen evolution at 62.5° are for nitrobenzene: 17.9 × 10^{-6} sec.$^{-1}$, for nitromethane: 13.4 × 10^{-6} sec.$^{-1}$.

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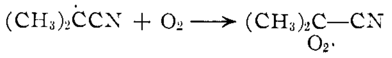
[18] G. S. Hammond, THIS JOURNAL, **72**, 3737 (1950); G. S. Hammond and L. H. Soffer, *ibid.*, **72**, 4711 (1950).

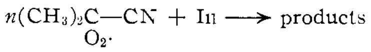
[19] M. C. Ford and W. A. Waters, *J. Chem. Soc.*, 1851 (1951).

used for the measurement of *a*. Decomposition of the products with the regeneration of iodine necessarily would have led to serious deviations from the observed zero-order rate of iodine disappearance.

The last method of estimating efficiencies was developed during the course of our study of the inhibition of the AIBN initiated air oxidation of hydrocarbons.[9] The immediate scavenger of initiator fragments in such reactions is oxygen. In the presence of powerful antioxidants the peroxy radicals thus produced are converted immediately to unreactive products.



$$(CH_3)_2\dot{C}CN + O_2 \longrightarrow (CH_3)_2\underset{O_2\cdot}{C}—CN \qquad (11)$$



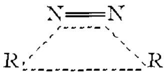
$$n(CH_3)_2\underset{O_2\cdot}{C}—CN + In \longrightarrow \text{products} \qquad (12)$$

The stoichiometric factor, *n*, which gives the number of radicals trapped by an inhibitor molecule has been determined on an absolute basis by the isolation of products derived from the inhibitors.[9] Good inhibitors give sharply defined induction periods which are proportional to the concentrations of the inhibitors. As with the other effective scavengers the knowledge of the lifetime of the inhibitors and their stoichiometric factors may be combined with the AIBN decomposition rates measured by nitrogen evolution to give values for the initiator efficiency. The results are included in Table II for comparison with the results of the iodine experiments. It will be noted that the agreement is excellent.

We are convinced that the agreement between the iodine and antioxidant methods is convincing evidence that the measurement of efficiencies of radical production from AIBN has been accomplished. The efficiency should, in general, be a function of the nature of the solvent alone. The only way in which deviation from this generalization could occur in properly controlled scavenging experiments is for radical pairs to undergo reaction with a scavenger before the pair is separated by diffusion. Such a reaction of styrene with radical pairs has been suggested by Matheson[20] but has fallen into disrepute with the recognition of the fact that the chain propagation step in styrene polymerization is not fast enough to compete with a diffusion controlled reaction.[21] It seems probable that such a reaction would have to involve either the reaction of both members of the radical pair with a bifunctional scavenger as in reaction 13 or the rapid formation of a molecular complex with one of the radicals.[22]

$$[2(CH_3)_2\dot{C}CN] + S \longrightarrow \text{non-radical products} \quad (13)$$

There is a second type of explanation for observed low efficiencies of radical production in AIBN decomposition. It is possible that the azonitrile can undergo a non-radical decomposition to give tetramethylsuccinonitrile directly with the extrusion of a nitrogen molecule. Such a reaction would necessarily involve a transition state such as II which would be closely related to the *cis*-azo compound.



II

It has been concluded[5] that the stable aliphatic azo compounds have the *trans* configuration. It would, therefore, be conceivable that the *trans* modification of AIBN undergoes isomerization to the *cis* at a rate which is comparable to the rate at which the former decomposes to give radicals. If the isomerization were rendered irreversible by the fast, non-radical decomposition it would be possible to account for all the kinetic behavior of AIBN. However, it is noteworthy that the efficiencies vary more with solvent than do the rates of decomposition. In order to maintain the total rates of decomposition nearly constant it would be necessary to adopt the view that the rates of the two independent processes vary in opposite ways to a compensating extent. This cannot be cited as a strong argument to distinguish between the two explanations of the measured inefficiency since it is not possible at this time to give a really adequate account of the solvent effects on the basis of either. We are continuing the study of this phase of the problem.

NOTE ADDED IN PROOF.—J. C. Bevington [*Nature*, **175**, 477 (1955)] reports a value of *ca.* 70% for the efficiency of radical production from AIBN in benzene at 60°. The determination involved the estimation, by isotopic dilution assay, of the tetramethylsuccinonitrile formed in the presence of DPPH. In view of the experimental errors likely to be involved in Bevington's method (*e.g.*, the yield of dinitrile formed in a control experiment with no scavenger seems lower than normally expected) we feel that the result is quite consistent with those reported above.

Acknowledgments.—We are indebted both to the Office of Naval Research and to the B. F. Goodrich Company for the support of these studies.

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(20) M. S. Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

(21) P. J. Flory, ref. 12, p. 121.

(22) G. S. Hammond and C. E. Boozer, THIS JOURNAL, **76**, 3861 (1954).