TABLE II

SYMMETRY SPECIES (C_{3h}), SELECTION RULES AND ASSIGNMENTS OF FUNDAMENTALS OF THE VIBRATIONAL SPECTRA OF TRISILYLAMINE AND TRISILYLAMINE-d_9

Description	A′ Raman	E′ Infrared and Raman	A″ Infrared	E″ Raman	Obsd. frequencies, cm.$^{-1}$ $(H_3Si)_3N$		$(D_3Si)_3N$	
					IR	R	IR	R
S–H stretching (d)[a]	ν_1	ν_7	ν_{14}	ν_{19}	2167	2140	1570	1556
Si–H stretching (s)[a]	ν_2	ν_8			2167	2140	1580	1556
SiH_3 deformation (d)	ν_3	ν_{10}	ν_{15}	ν_{20}	944	..	698	..
SiH_3 deformation (s)	ν_4	ν_{11}			944	..	698	..
SiH_3 rocking	ν_5	ν_{12}	ν_{16}	ν_{21}	748	..	587	..
SiH_3 torsion			ν_{18}	ν_{22}	..	..	..	..
N–Si stretching	ν_6					490		459
N–Si stretching		ν_9			996	..	963	..
NSi_3 deformation		ν_{13}			(250)	..	(250)	..
NSi_3 deformation			ν_{17}		..		..	

[a] "Degenerate" and "symmetric" with respect to the 3-fold axis of the silyl group.

Bands arising from the stretching, deformation and rocking of the silyl groups are, as they were in disiloxane, clumped together in three regions of absorption which show no structure except for the apparent doubling of the Si–D stretching band in heavy trisilylamine. This latter has been interpreted as a separation of the symmetric and "degenerate" stretching of the isolated silyl groups.

The overtones and combinations are assigned with fair satisfaction. Aside from those already discussed the only one that completely evades explanation is that at 1389 cm.$^{-1}$ in the light compound. It may be due to an impurity. The two ternary combinations in the heavy compound are assigned with skepticism, but better guesses have not been made and it is not felt that any of these can be used with confidence to estimate ν_{17}.

NOTE ADDED IN PROOF.—Subsequent far infrared work on disiloxane (340 mm. with a 20-cm. path) between 180 and 270 cm.$^{-1}$ has failed to confirm the apparent absorption near 250 cm.$^{-1}$ mentioned above as showing on Perkin–Elmer spectra. Since the appearance of these traces is similar to that of the trisilylamine spectra, one is forced to distrust the above estimate of ν_{13}. Unfortunately, at the time of publication, available samples of the amine will not fill our large far infrared cell to a pressure greater than 35 mm. At this pressure there is no absorption between 180 and 270 cm.$^{-1}$ strong enough to be unambiguously assignable to a fundamental.

Acknowledgments.—The interest and efforts of Messrs. E. D. Eanes and J. Hardin in obtaining Raman spectra are gratefully acknowledged. The construction of the far infrared spectrometer was made possible by a generous grant from the National Science Foundation.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dead-end Radical Polymerization

BY ARTHUR V. TOBOLSKY

RECEIVED MAY 16, 1958

When radical initiators are used to initiate the polymerization of vinyl monomers, and if there is no retardation of termination at high conversions, the polymerization ceases short of complete conversion. In certain cases the limiting conversion may be very low. A complete theoretical treatment is given for the case of initiation with 2-azobisisobutyronitrile. The results are worked out in detail for this initiator in styrene at 100°.

Introduction

The radical initiated polymerization of vinyl monomers has certain complicating features at high conversions, such as the retardation of the termination steps observed in methyl methacrylate.[1] This apparently has discouraged thorough theoretical treatment of high conversion phenomena. However, many monomers such as styrene show a quite minor Tromsdorff–Norrish effect.

One phenomenon is of particular interest: when fast initiators are used in styrene at moderate temperatures the polymerization stops at quite low conversions. Such readily can be observed with initiating systems such as benzoyl peroxide–dimethylaniline or methyl ethyl ketone peroxide–cobalt naphthenate. We may term this phenomenon "dead-end polymerization." With the initiating systems mentioned above a complicating feature is possible wasteful reactions in which the activator destroys the peroxide by side reactions which do not start polymer chains.

An initiator that has been very thoroughly investigated and for which wasteful side reactions do not occur is 2-azobisisobutyronitrile.[2] The question is: can dead-end polymerization be observed with this initiator? The answer, quite surprisingly, is yes.

Theoretical

The rate of radical initiated vinyl polymerization, initiated by a catalyst of concentration [Cat], is given by

$$-\frac{d[M]}{dt} = k_p[C^*][M] \qquad (1)$$

$$-\frac{d[M]}{dt} = \frac{k_p}{k_t^{1/2}} k_d^{1/2} f^{1/2} [Cat]^{1/2} [M] \qquad (2)$$

In equation 2 we are disregarding the polymer produced by the purely thermal polymerization. In these equations [M] represents the concentration of unreacted monomer, [Cat] the concentration of unreacted catalyst, f is the catalyst effi-

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(1) E. Tromsdorff, H. Kohle and P. Lagolly, *Makromol. Chem.*, **1**, 169 (1948); R. G. W. Norrish and R. R. Smith, *Nature*, **150**, 336 (1942).

(2) The *C.A.* name is 2,2′-azobis-(2-methylpropionitrile).

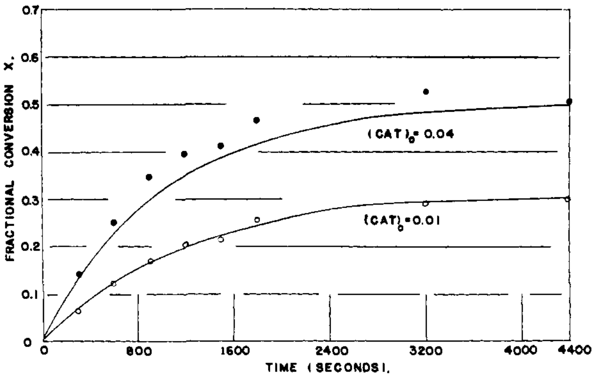

Fig. 1.

ciency, that is the fraction of radicals produced by the primary cleavage of catalyst that actually start polymer chains. The rate constant k_d is the rate constant for the first-order primary cleavage of catalyst, k_p is the specific rate of propagation, $k_t = k_{tc} + k_{td}$ the sum of the specific rates of combination and disproportionation, respectively. The notation is in fairly wide usage.[3]

If the catalyst is 2-azobisisobutyronitrile, the rate of disappearance of catalyst is given by

$$-\frac{d[\mathrm{Cat}]}{dt} = k_d[\mathrm{Cat}] \qquad (3)$$

if the initial concentration of catalyst is $[\mathrm{Cat}]_0$ and if the catalyst is all added at the beginning of the polymerization, one obtains

$$[\mathrm{Cat}] = [\mathrm{Cat}]_0\, e^{-k_d t} \qquad (4)$$

Substituting equation 4 into equation 2 and integrating, one obtains successively

$$-\frac{d[\mathrm{M}]}{[\mathrm{M}]} = \frac{k_p f^{1/2} k_d{}^{1/2}}{k_t{}^{1/2}} [\mathrm{Cat}]_0{}^{1/2} e^{-k_d t/2}\, dt \qquad (5)$$

$$-\ln\frac{[\mathrm{M}]}{[\mathrm{M}]_0} = \frac{2k_p}{k_t{}^{1/2}} \frac{f^{1/2}[\mathrm{Cat}]_0{}^{1/2}}{k_d{}^{1/2}} (1 - e^{-k_d t/2}) \qquad (6)$$

In equation 6 $[\mathrm{M}]_0$ is the initial concentration of monomer. (I shall use the concentration unit of moles/liter and the time unit of seconds throughout.)

It is interesting to note that [M] reaches a limiting value $[\mathrm{M}]_\infty$ when $t \rightarrow \infty$

$$-\ln\frac{[\mathrm{M}]_\infty}{[\mathrm{M}]_0} = \frac{2k_p}{k_t{}^{1/2}} \frac{f^{1/2}[\mathrm{Cat}]_0{}^{1/2}}{k_d{}^{1/2}} \qquad (7)$$

or

$$-\ln\,[1 - x_\infty] = \frac{2k_p}{k_t{}^{1/2}} \frac{f^{1/2}[\mathrm{Cat}]_0{}^{1/2}}{k_d{}^{1/2}} \qquad (7a)$$

$$x_\infty = ([\mathrm{M}]_0 - [\mathrm{M}]_\infty)/[\mathrm{M}]_0$$

Very fortunately the quantities k_d,[4] $k_p/k_t{}^{1/2}$[5] and f[6] are all quite accurately known for 2-azobisisobutyronitrile and styrene over a wide range of temperature. For the case of styrene $k_{td} = 0$, so that the quantity

$$A' = (2k_{td} + k_{tc})/k_p{}^2 = (k_{tc} + k_{td})/k_p{}^2 = k_t/k_p{}^2$$

A' has been very accurately determined,[5] and the value of $k_p/k_t{}^{1/2}$ at 100° = 0.0915. The value of k_d for 2-azobisisobutyronitrile at 100° is 1.60×10^{-3} sec.$^{-1}$. The value of f, the catalyst efficiency was found to be 0.60 at a number of temperatures and should be independent of conversion up to very high conversions. The half-life is 435 seconds.

If one selects initial catalyst concentrations $[\mathrm{Cat}]_0$ such as 0.01 and 0.04 mole/liter, equation 6 should allow one to predict the course of the catalyst initiated conversion of styrene at 100° without any adjustable parameters. This has been done in Fig. 1. It must be pointed out that purely thermal polymerization of styrene, while small in the time scale shown in Fig. 1, should be corrected for when comparing theory with experiment. The ordinate in Fig. 1 is fractional conversion, x

$$x = ([\mathrm{M}]_0 - [\mathrm{M}])/[\mathrm{M}]_0 \qquad (8)$$

The points shown in Fig. 1 were actual experimental points at the indicated catalyst concentrations. These experimental points were corrected for thermal polymerization merely by substracting the measured thermal conversion in a thermal polymerization of the same sample of styrene at 100°. This procedure is quite valid at the longer times, when the initiator in the catalyzed run has disappeared. At smaller time values this method is not exact[7] but the amount of thermal polymerization is so small, about 2% per hour, in comparison with the catalyzed polymerization, that this procedure is sufficiently accurate.

The limiting conversion predicted from equation 7 at $[\mathrm{Cat}]_0 = [0.01]$ is 0.30; at $[\mathrm{Cat}]_0 = [0.04]$ the predicted limiting conversion is 0.51. This is in excellent accord with the experimental facts. Indeed the agreement between theory and experiment over the entire range is reasonably good, considering that the theoretical curves were completely predicted without any adjustable parameter before the experimental results were obtained.[8]

Size Distribution

For simplicity we shall neglect the effect of chain transfer to monomer, which is small in styrene.

Since termination by combination is operative in styrene, the size distribution of the polymer *instantaneously formed* is characterized by[9] $\bar{P}_w/\bar{P}_n = 1.5$. The value of $\bar{P}_n$ of the *initially* formed polymer is

$$\bar{P}_n = \frac{k_p[\mathrm{M}]_0}{k_t{}^{1/2} k_d{}^{1/2} f^{1/2} [\mathrm{Cat}]_0{}^{1/2}} \qquad (9)$$

the cumulative values of $\bar{P}_n$ at the dead-end of the polymerization is

$$\bar{P}_n\,(\text{cumulative-final}) = \frac{[\mathrm{M}]_0 - [\mathrm{M}]_\infty}{f[\mathrm{Cat}]_0} \qquad (10)$$

The term in the numerator is the moles of monomer per liter incorporated in polymer. The term in the denominator is the moles of polymer molecules, since there are 2 $f[\mathrm{Cat}]_0$ moles/liter of catalyst fragments at the ends of polymer chains and 2 catalyst fragments per molecule.

The cumulative value of $\bar{P}_n$ at any time is given by

$$\bar{P}_n\,(\text{cumulative}) = \frac{[\mathrm{M}]_0 - [\mathrm{M}]}{f([\mathrm{Cat}]_0 - [\mathrm{Cat}])} \qquad (11)$$

where [M] and [Cat] can be obtained from equation 6 and 4, respectively. The cumulative $\bar{P}_w$ is given by the formula

$$\bar{P}_w\,(\text{cumulative}) = \int_{[\mathrm{M}]}^{[\mathrm{M}]_0} \frac{1.5}{f} \frac{d([\mathrm{M}]}{d[\mathrm{Cat}]} \frac{d[\mathrm{M}]}{[\mathrm{M}]_0 - [\mathrm{M}]} \qquad (12)$$

The quantity d(M)/d[Cat] can be obtained explicitly as a function of [M] from equations 3, 4, 5 and 6 so that equation 12 is an explicit quadrature.

Discussion

It is well known as a practical matter that in the catalyzed polymerization of styrene at high temperatures it is difficult to polymerize the last traces of monomer. This is usually regarded as a diffusion effect. However, in the light of equations 6 and 7 this may in many cases also be due to depletion of catalyst. At very high conversions the thermal rate is slow even at high temperatures because the rate of initiation for thermal polymerization is probably third order.[10]

It would appear from equation 7a that a limiting conversion short of unity is reached under all conditions (neglecting thermal polymerization). This limiting conversion can be exceedingly close to unity if the right-hand side of equation 7a is a large number, and quite small if the right-hand side of equation 7a is a small number. The most impor-

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(3) F. R. Mayo, R. A. Gregg and M. S. Matheson, THIS JOURNAL, **73**, 1691 (1951).

(4) J. P. Van Hook and A. V. Tobolsky, *ibid.*, **80**, 779 (1958).

(5) J. Offenbach and A. V. Tobolsky, *J. Polymer Sci.*, **16**, 311 (1955).

(6) J. P. Van Hook and A. V. Tobolsky, *ibid.*, (in press).

(7) A. V. Tobolsky, *Ann. Rev. Phys. Chem.*, **7**, 167 (1956).

(8) The experimental results were obtained at my request by my associate Dr. Charles E. Rogers to whom I extend my sincere thanks.

(9) A. V. Tobolsky and B. Baysal, *J. Polymer Sci.*, **9**, 171 (1952).

(10) F. R. Mayo, THIS JOURNAL, **75**, 6133 (1953).

tant magnitude is $k_p/(k_t k_d)^{1/2}$, which is determined at any temperature by the nature of the monomer and the initiator.

Equations 6 and 7 may also be very useful for kinetic studies. If k_d is known, as for 2-azobisisobutyronitrile, these equations, may be used to obtain $(k_p/k_t^{1/2})f^{1/2}$. If k_d and $(k_p/k_t)^{1/2}$ are known, the efficiency f can be found. Equation 6 can readily be put into the form

$$\frac{\ln(1 - x)}{\ln(1 - x_\infty)} = 1 - e^{-k_d t/2} \qquad (13)$$

A determination of x as a function of time, including the asymptotic value x_∞, immediately gives a value for k_d from equation 13.

The phenomenon of dead-end polymerization can be treated in more complex cases, where the disappearance of catalyst is not simply given by equation 3 but by an equation such as

$$-\frac{d[\mathrm{Cat}]}{dt} = k_d\,[\mathrm{Cat}] + k_i\,[\mathrm{Cat}]^{\nu} \qquad (14)$$

where the second term on the right-hand side refers to induced decomposition. This situation would apply to benzoyl peroxide. The mathematical treatment is obviously more complex.

The treatment is very simple if we have an activated system where destruction of catalyst is given by

$$-\frac{d[\mathrm{Cat}]}{dt} = k_d'[\mathrm{Cat}][\mathrm{Act}] \qquad (15)$$

and the initiation of polymer chains is given by

$$R_i = f'k_d'[\mathrm{Cat}][\mathrm{Act}] \qquad (16)$$

In equations 15 and 16 [Act] represents activator concentration and f' represents initiator efficiency.

PRINCETON, NEW JERSEY

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER]

The Photolyses of 2-Pentanone and 2-Pentanone-1,1,1,3,3-d_5[1]

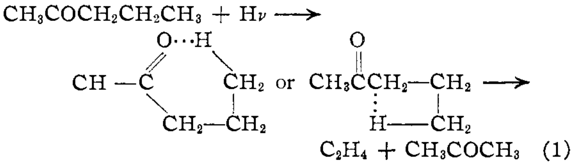
BY P. AUSLOOS AND E. MURAD

RECEIVED JUNE 18, 1958

The photolyses of 2-pentanone and 2-pentanone-1,1,1,3,3-d_5 have been investigated at long wave lengths at maximum intensity of 3.7×10^{14} quanta/cc./sec. and at short wave lengths. This investigation was carried out in the temperature range 25–83°. In this study, ethylene was found to be, within experimental error, equal to the acetone yield. In the experiments with the deuterated ketone, 90% of the acetone formed was acetone-d_5. Secondary reactions are discussed and certain ratios of rate constants are deduced.

Introduction

Ketones containing at least one hydrogen atom in the γ-position dissociate photochemically into olefins and simple ketones.[2] As pointed out by Nicholson[3] the formation of 1-butene in the photolysis of methyl *n*-amyl ketone is evidence for the fact that a γ-hydrogen is involved in the molecular rearrangement process. This intramolecular rearrangement process has been visualized to take place *via* the formation of a ring intermediate. Taking 2-pentanone as an example, this process can be written as



$CH_3COCH_2CH_2CH_3 + H\nu \longrightarrow$ … $\longrightarrow C_2H_4 + CH_3COCH_3$ (1)

However, in a recent study of the photochemical decomposition of 2-pentanone-1,1,1,3,3-d_5[4] it was found that over a wide intensity and temperature range more CD_3COCD_3 was produced than CD_3COCD_2H, and that at high intensities the ethylene/acetone ratio was higher than unity. Because these observations could not be explained by a process such as I, a different interpretation was presented, whereby, depending on the intensity, the excited ketone molecules reacted either with excited or with normal molecules.

In the present work the short and long wave length vapor phase photochemical decompositions of 2-pentanone and 2-pentanone-1,1,1,3,3-d_5 have been investigated at low temperatures and at intensities higher than those used in previous studies of these compounds. In a few photolyses oxygen was added to gain increased knowledge of the primary process.

Experimental

Irradiation.—The long wave length runs were made with an unfiltered Hanovia S-100 medium pressure mercury lamp. The light was collimated into the cell with one short focus lens. The distance between the lamp and the front window of the cell was approximately 6 cm. In most experiments the intensity was increased by irradiating the opposite end of the cell with a second Hanovia S-100 lamp. The volume of the cell was 195 ml. (10 cm. long and 5 cm. in diameter). The temperature of the cell was controlled by a constant temperature bath provided with double quartz windows and filled with distilled water. The number of quanta absorbed was determined by measuring the carbon monoxide yield in the photolysis of diethyl ketone at 90°.

The short wave length runs were carried out with a Hanovia hydrogen discharge lamp. The cell was placed at a distance of about 2 cm. from the lamp. At the low pressures used in these experiments, practically all of the absorbed radiation lies near 1900 Å. No attempt was made to determine the absorbed light intensity.

Analysis.—The carbon monoxide–methane fraction was removed at liquid nitrogen temperature and analyzed over hot CuO. The C_2 fraction was removed at −157°. The C_3 and C_4 fractions were separated at −135° and at −110°, respectively. All fractions were analyzed mass spectrometrically. Hexane, acetone, biacetyl and the parent compound were separated on a Perkin–Elmer Vapor Frac-

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[1] This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under contract No. AF(600)-1528. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] For a review see: J. N. Pitts, Jr., *J. Chem. Educ.*, **34**, 112 (1957).

[3] A. J. C. Nicholson, *Trans. Faraday Soc.*, **50**, 1067 (1954).

[4] J. R. McNesby and A. S. Gordon, THIS JOURNAL, **80**, 261 (1958).