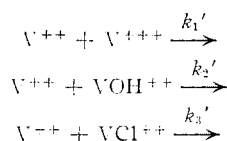


Discussion

A plausible interpretation of the three-term rate expression, equation 4, is that exchange can occur *via* the three paths



If there is rapid equilibrium between the various vanadium(III) species, a questionable assumption for solutions containing chloride ion (see Results) and possibly even for the solutions of low acidity, and if most vanadium(III) is present as V^{+++} , a good approximation for the solution studied, $k_1' = k_1$, $k_2' = k_2/K_h$, and $k_3' = k_3/K_c$, K_h being $(VOH^{++})(H^+)/(V^{+++})$ and K_c being $(VCl^{++})/(V^{+++})(Cl^-)$ under the conditions of the experiments.

Furman and Garner²⁷ use a value of $K_h = 2 \times 10^{-3} M$ for conditions similar to ours, but near ionic strength 1.2. Taking this same value as approximately correct for our conditions, $k_2 = \sim 10^5 M^{-1} \text{ min.}^{-1}$.

The value of K_c is unknown. Furman and Garner²⁸ reported that greater than a twenty-fold excess of chloride ion over vanadium(III) was required to change the vanadium(III) spectrum appreciably.

As shown in Table III the rate of exchange between V^{++} and V^{+++} is greater than the rate of electron exchange between Cr^{++} and Cr^{+++} or between Eu^{++} and Eu^{+++} but less than that between Fe^{++} and Fe^{+++} . The rate of exchange between Co^{++} and Co^{+++} has not been determined, but in 1 *f* $HClO_4$ at 0° the over-all rate of exchange⁷ between Co^{II} and Co^{III} is approximately equal to the

(27) S. C. Furman and C. S. Garner, *THIS JOURNAL*, **74**, 2333 (1952).

(28) S. C. Furman and C. S. Garner, *ibid.*, **72**, 1789 (1950).

TABLE III

COMPARISON OF EXCHANGE RATES

(Values are specific rate constants at 25° in units of $M^{-1} \text{ sec.}^{-1}$)

System	Ionic strength	$M^{++} + M^{+++}$	$M^{++} + MOH^{++}$	$M^{++} + MCl^{++}$
$Fe^{II}-Fe^{IIIa}$	0.55	4.2	3200	37
$V^{II}-V^{IIIb}$	2.0	1.0×10^{-2}	~ 1.8	$\sim 1.4/K_c$
$Cr^{II}-Cr^{IIIc}$	1.0	$< 2 \times 10^{-5}$	~ 0.7	10 (0°)
$Eu^{II}-Eu^{III d}$	2.0	$< 1 \times 10^{-4}$...	$3.7 \times 10^{-4}/K_c'$

^a Reference 5. ^b This paper. ^c Ref. 2, 3 and 4. ^d Reference 8.

over-all rate of exchange between Fe^{II} and Fe^{III} under similar conditions.⁵

For the $Eu^{++}-Eu^{+++}$ exchange a 4f electron is transferred, but for each of the other reactions a 3d electron is transferred and so these reactions are similar both as to charge type and type of electron transferred. If the slowness of exchange between Cr^{++} and Cr^{+++} is associated with the non-lability^{29,30} of the first coordination sphere about Cr^{+++} , a situation that would hinder exchange *via* electron transfer because of Franck-Condon restrictions^{31,32} and also exchange *via* a bridged activated complex,^{3,33} then the $V^{++}-V^{+++}$ exchange might also be hindered for similar reasons since V^{++} and Cr^{+++} are iso-electronic. Preliminary experiments,³⁴ however, indicated that O^{18} exchange between H_2O and the hydrated V^{++} ion was complete in $< \sim 10$ minutes at 0° . There was some evidence, although not conclusive, that exchange was incomplete in ~ 1 minute at 0° .

(29) R. A. Plane and H. Taube, *J. Phys. Chem.*, **56**, 33 (1952).

(30) H. Taube, *Chem. Revs.*, **50**, 99 (1952).

(31) W. F. Libby, *J. Phys. Chem.*, **56**, 863 (1952).

(32) B. J. Zwolinsky, R. J. Marcus and H. Eyring, *Chem. Revs.*, **55**, 157 (1955).

(33) H. Taube, H. Meyer and R. L. Rich, *THIS JOURNAL*, **75**, 4118 (1953).

(34) B. Keisch and Kotra V. Krishnamurty, reported in reference 1.

SAINT LOUIS, MISSOURI

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE JOHNS HOPKINS UNIVERSITY]

The Vibrational Spectra of Trisilylamine and Trisilylamine- d_9

BY DEAN W. ROBINSON

RECEIVED JUNE 16, 1958

The infrared spectra between 4000 and 60 cm.^{-1} of trisilylamine and trisilylamine- d_9 are reported as well as some Raman data. The observed spectra are interpreted on the basis of a C_{3h} point group with three of the four skeletal frequencies observed at 996, 490 and *ca.* 250 cm.^{-1} in trisilylamine and 963, 459 and *ca.* 250 cm.^{-1} in trisilylamine- d_9 . Silicon-hydrogen motions group together at three silyl-group frequencies in the regions 2167, 944 and 748 cm.^{-1} in the light compound and 1575, 698 and 587 cm.^{-1} in heavy trisilylamine.

Structural studies of silyl Lewis bases indicate large bond angles, shorter bond lengths and higher force constants than are expected from comparison with methyl compounds. Aside from the well-known short bond distances in silyl halides, there is evidence¹ for a much greater bond angle in disiloxane than in dimethyl ether, although its exact

(1) R. C. Lord, D. W. Robinson and W. C. Schumb, *THIS JOURNAL*, **78**, 1327 (1956). See also R. F. Curl and K. S. Pitzer, *ibid.*, **80**, 2371 (1958), who studied $H_3SiOSiH_3$ in matrices at $20^\circ K$. Their interpretation of their data is questionable but yields an $SiOSi$ angle of $150-158^\circ$ in the solid phase, an unexpectedly wide angle in agreement with the previous investigators.

angle has not yet been reported. Trisilylamine on the other hand has been the subject of a careful electron diffraction investigation by Hedberg² and has been shown to have $Si-N-Si$ bond angles of $119.6 \pm 1.0^\circ$, a nearly planar skeletal structure.

The present paper is a description of some vibrational spectroscopic work that has given results in agreement with the electron diffraction study, that is, that trisilylamine is indistinguishable from a C_{3h} molecule.

(2) K. Hedberg, *ibid.*, **77**, 6491 (1955).

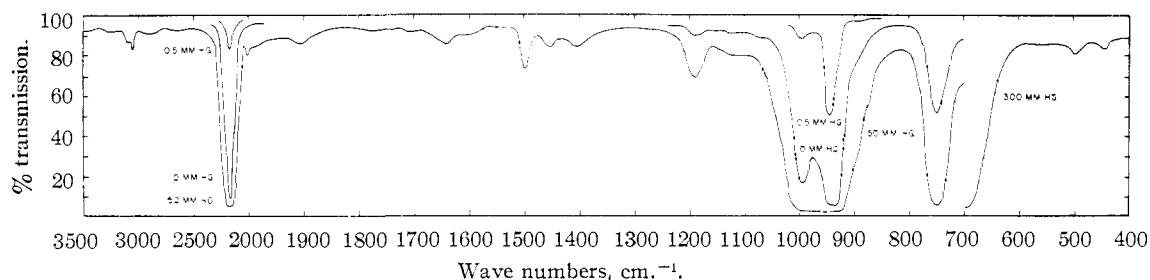
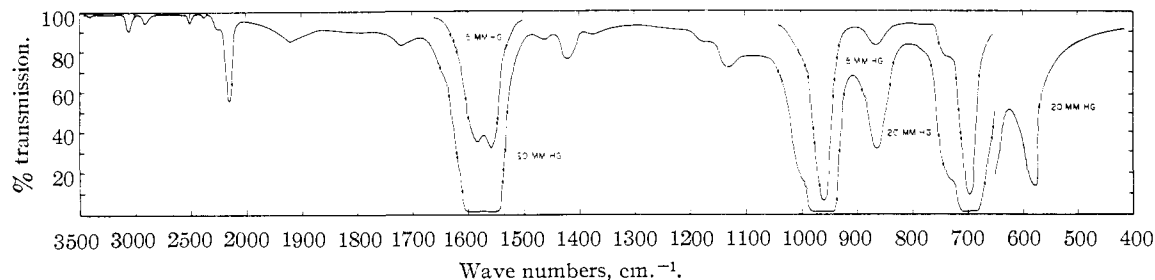


Fig. 1.—The infrared spectrum of trisilylamine.

Fig. 2.—The infrared spectrum of trisilylamine- d_9 .

Experimental

Preparation of Samples.—Trisilylamine was prepared by the classical method of Stock and Somieski³ in which excess monochlorosilane is allowed to react at room temperature with dry ammonia. Contaminants more volatile than trisilylamine were separated by slow vacuum fractional condensation through traps immersed in carbon disulfide slush, and impurities less volatile than trisilylamine were removed by fractionation through traps immersed in a trichloroethylene–Dry Ice slush. The chlorosilane was prepared by the operation⁴ of heating silane and HCl to 100° for 20–30 hours in the presence of aluminum chloride in a large sealed flask, then separating the omnipresent dichlorosilane from monochlorosilane by fractionation through a trap immersed in carbon disulfide slush. Pennsylvania Salt Co. ammonia was dried by distillation from a concentrated sodium solution.

The fully deuterated compound was prepared in exactly the same way using LiAlD_4 , then DCl for the chlorination. The aminolysis of chlorosilane- d_3 was made with light ammonia.

Determination of Spectra.—Infrared spectra of the gaseous compounds were obtained with a Perkin-Elmer model 21 double-beam spectrophotometer equipped with sodium chloride and cesium bromide optics. Ten centimeter gas cells were used throughout with sodium chloride and KRS-5 windows in the appropriate regions. Pressures up to the vapor pressure of trisilylamine at room temperature (ca. 320 mm.) were used. Spectra in the NaCl region were calibrated with a polystyrene film and band centers, estimated from the point of minimum transmission, are reliable to the usual limits of the instrument. Prism spectra were run of trisilylamine at 77°K. condensed in a CO_2 matrix through the NaCl and CsBr regions. Far infrared spectra were determined with a large grating spectrometer⁵ through the region of 230 to 60 cm^{-1} . An 8 cm. gas well with polyethylene windows, doubly passed, was used for this work.

Raman spectra were obtained on liquid samples using the 4358 Å. mercury line and filtering with 1 cm. thickness of a 0.075 g./l. rhodamine-g solution and saturated sodium nitrite. Spectrographs used were a Hilger quartz prism instrument of dispersion about 56 Å./mm. and a fast grating spectrograph of 8 Å./mm. dispersion at the wave length used. Exposure times of the order of eight to ten hours were necessary on the grating spectrograph as the physical dimensions of the Pyrex-enclosed samples were only about 3 mm. diameter by 2 cm. long. The source consisted of six General

Electric A-H2 mercury lamps surrounded by a magnesium oxide reflector. The spectra obtained were rather disappointing as the source was not very intense, the compound is a weak scatterer, the samples were small and the long exposure times produced considerable continuous blackening of the plates. Halation about the exciting line was quite low and weak grating ghosts as low as 31 cm^{-1} away were easily observed. Reported shifts are good to 2 cm^{-1} .

Results and Discussion

The infrared spectra are exceedingly simple for a molecule containing 13 atoms. This results from its high symmetry and the fact that modes involving principally silicon-hydrogen motions are only weakly coupled through the skeleton producing a great deal of over-lapping which the instrument available was not able to resolve.

The spectra are interpreted on the assumption of C_{3h} symmetry.⁶ All observed infrared bands are listed in Table I along with their assignments. The numbering of the fundamentals together with qualitative descriptions of the modes of vibration, and the observed frequencies are set down in Table II. Figures 1 and 2 display the infrared spectra.

Most of the observed bands in the spectra can be satisfactorily accounted for, although not all of the normal frequencies can be placed with certainty at the present time. Most of the fundamentals are quite broad and not only were the symmetric and "degenerate" stretching and deformation vibrations of isolated silyl groups unresolvable, but pairs belonging to different species of C_{3h} could not be separated. None of this is very surprising considering that this was also the case with disiloxane, a molecule whose spectrum¹ is almost identical in all of its features to that of trisilylamine. Upper stage bands due to low frequency fundamentals as well as unresolved Fermi resonances arising from the rather weak mechanical coupling between silyl groups probably serve to broaden bands and prevent resolution of some of the overlapping hydrogen frequencies. The differences noted between Raman and infrared values of the Si–H and Si–D stretching frequencies undoubtedly are due only to the difference in state of aggregation.

(6) Actually it would be just as sensible to assume a D_{3h} molecular point group which the molecule would exhibit if the silyl groups rotated freely. This would not, however, affect any of the results of this paper and nothing can be said about the restriction of this motion.

(3) A. Stock and K. Somieski, *Ber.*, **54**, 740 (1921).

(4) A. Stock and K. Somieski, *ibid.*, **52**, 695 (1919).

(5) To be described elsewhere.

TABLE I
OBSERVED FREQUENCIES AND ASSIGNMENTS

Assignment	Frequency H, cm. ⁻¹	Frequency D, cm. ⁻¹
ν_{13}	ca. 250m	ca. 250m
$\nu_{10} - \nu_6, \nu_{11} - \nu_6, \nu_{15} - \nu_6$, etc.	446v vw	
$2\nu_{13}?$	500v vw	
H ₃ SiCl impurity	557vw	540vw
ν_{12}, ν_{16}	748m	587m
$\nu_{10}, \nu_{11}, \nu_{15}$	944vs	698vs
-SiD ₂ H impurity rock		734m
-SiD ₂ H impurity def.		865m
ν_9	996s	963vs
Si-O-Si impurity	1105v vw	
?	1185w	1133w
?	1389v	
$\nu_6 + \nu_{10}, \nu_6 + \nu_{11}, \nu_6 + \nu_{15}$	1441vw	1170vw
$\nu_6 + \nu_9$	1490w	1423w
impurity ?	1639vw	
$2\nu_{13} + \nu_9$		1466vw
$\nu_3 + \nu_{10}, \nu_3 + \nu_{11}$, etc.	1900vw	1380vw
$\nu_3 + 2\nu_{12}, 3\nu_{12}$, etc. ?		1727w
$2\nu_9$	2005w	1927w
ν_7, ν_{14}	2167s	1570s
ν_8	2167s	1580s
SiD ₂ H impurity		2165m
$\nu_1 + \nu_{12}, \nu_1 + \nu_{16}$, etc.	2890v vw	
$\nu_1 + \nu_{10}, \nu_1 + \nu_{11}$, etc.	3110w	2262vw
$\nu_1 + \nu_9, \nu_7 + \nu_9$, etc.	3175vw	2510vw
$\nu_1 + \nu_7, \nu_1 + \nu_{14}$, etc.	ca. 4250v vw	ca. 3080vw

One sees from the selection rules for the point group C_{3h} given in Table II that since the hydrogen and deuterium motions of different symmetries are not separated, the only fundamental that could not be observed or closely estimated from infrared data alone is the NSi_3 , A' stretching motion. Fortunately this gives the second strongest line in the Raman spectrum and, in spite of the difficulties in obtaining good plates, shows through clearly at displacements of 490 and 459 cm^{-1} for the hydrogen and deuterium compounds, respectively. These lines are sharp, characteristic of totally symmetric vibrations, and the isotopic shift is about right for a skeletal frequency. Assuming a four particle system the frequency of this mode in the deuterium compound should be 468 cm^{-1} (using the Si-N stretching constant of 4.4×10^5 dynes/cm. based on the 490 cm^{-1} observed frequency in the light compound). This is the only A' skeletal motion so the assignment seems fairly unambiguous.

The E' skeletal stretching mode is assigned to the strong infrared band at 996 cm^{-1} in the hydrogen compound and 963 in the deuterium compound; this is mainly by analogy to the antisymmetric stretch in silicon-oxygen-silicon compounds.¹ These lie about 120 cm^{-1} lower than the oxygen analogs.

The two remaining skeletal modes of vibration are a degenerate deformation and an A'' bending motion. The E' deformation is assigned to a very broad band at the end of the useful CsBr region. Absorption in this vicinity slowly increases from about 300 cm^{-1} out to the limit of the prism, 250 cm^{-1} , in the light and heavy compounds so that the center of the band cannot be measured with much certainty. Our grating spectrometer with the grating available at present, employed in the second order, cannot be used with confidence at frequencies much above 200 cm^{-1} and, although samples of trisilylamine and disiloxane were run while trying to stretch the high frequency region back to 250 cm^{-1} , no absorption was detected. This may mean that the energy detected at frequencies above 200 cm^{-1} was due in part to other orders and any broad absorption of the second-order component was just not sufficiently different from the empty cell spectra to be observed. A new grating to be acquired soon should clear up this uncertainty.

A frequency of 250 cm^{-1} will be taken tentatively for this band. The mode would be expected to have a frequency

similar to that of the Si-O-Si bending fundamental of disiloxane¹ and spectra of disiloxane taken with the CsBr prism show the same broad band at or around 250 cm^{-1} . This will also be subjected to closer investigation in the future. Neither trisilylamine at 100 mm. nor disiloxane at 500 mm. with 16 cm. path length shows any other absorption out to 60 cm^{-1} , so that if this band near 250 cm^{-1} has been misinterpreted, the bending motion in question must be at some frequency below this. Such a possibility might not, however, be unreasonable in view of the well-known weakly directional characters of Si-O-Si and presumably Si-N-Si linkages with their concomitantly weak bending potential constants.

There still remains one skeletal fundamental the frequency of which cannot be estimated. This is the A'' motion of the nitrogen passing through the plane of the silicon atoms. One might speculate that such a motion would take place with greater frequency than the degenerate deformation. In fact, assuming again a four-particle system, and further taking the potential constant for this motion to be about 2.5 times the potential constant for the in-plane bending⁷ calculated from the 250 cm^{-1} frequency, one expects the A'' bending to have a frequency between 450 and 500 cm^{-1} . Specifically the substantial agreement between the fundamentals of BCl_3 , 471 (a_1'), 462 (a_2''), 958 (e') and 243 (e') and the known skeletal modes of trisilylamine support this estimate of the A'' bending vibration. An examination of the spectra in this region turns up hardly a trace of absorption except for an extremely weak band at 446 cm^{-1} in the hydrogen compound which does not have a counterpart in the spectrum of deuterium compound. If the A'' bending motion does take place with a frequency of between 450 and 500 cm^{-1} , the reason for missing it is not clear. The very weak band at 446 cm^{-1} disappears on cooling to -196° in a CO_2 matrix and fits the assignment as a difference band fairly well. The very weak band at 500 cm^{-1} has a counterpart in disiloxane at 505 cm^{-1} so it is probably not due to the A'' bending. The band conceivably could fall at about 750 cm^{-1} and be obscured by silyl rocking in the hydrogen compound and silyl deformation in the deuterium compound, but this seems rather high for such a motion. One would expect high transition probability for such a fundamental which could only vanish if the Si-N bond moments are close to zero. In view of the back-coordination of the p- π electrons of nitrogen into the 3-d orbitals of silicon,⁸ such an effect is not out of the question.

One further point of interest in connection with the skeletal motions is the weak band at 1185 cm^{-1} which shifts to 1133 cm^{-1} in the heavy compound. Seemingly analogous bands are observed in disiloxane¹ as well as such compounds as $F_3SiOSiF_3$, $Cl_3SiOSiCl_3$ and $[(H_3C)_3Si]_2O$.⁹ Spectra have been obtained in this Laboratory of solid trisilylamine at liquid nitrogen temperature and solid disiloxane, the latter both pure and in a carbon tetrachloride matrix. Although the unexplained bands at 1220 cm^{-1} in disiloxane and 1185 cm^{-1} in trisilylamine look alike at 300°K. and behave similarly on deuterium substitution, the band in disiloxane disappears on cooling to 77°K. while that in trisilylamine does not decrease in intensity. It is extremely hazardous to base much of an argument upon a comparison of the gaseous and solid spectra, as striking changes take place on solidification, at least at 77°K.,¹⁰ but the evidence suggests that these bands may not be due to similar combinations and although that in disiloxane appears to be a difference band, that in trisilylamine may be a summation frequency. The assignment of neither of these has as yet been made.

(7) This assumption arose through comparison of similar constants for BF_3 , BCl_3 , BBr_3 , CO_2 , and NO_2 as quoted by G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., New York, N. Y., 1945, p. 178.

(8) This suggestion has been made several times in the literature. Theoretical justification is found in D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332 (1954).

(9) Work done in this Laboratory.

(10) The appearance of new bands and the splitting and large shifts of old ones on solidification is strongly suggestive of association. Such association might be expected as silicon behaves as a Lewis acid in many cases. Witness, for example, the chemical and physical properties of $(CH_3)_2(SiH_2)N$ (S. Sujishi and S. Witz, *This Journal*, **79**, 2447 (1957)) pointing toward intermolecular association and the well-known ability of silicon halides to form stable addition compounds with amines.

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}			
					IR (H_3Si) $_3N$	R	IR (D_3Si) $_3N$	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

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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

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

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

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-

(1) E. Tromsdorff, H. Köhle 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).