identical isotope effects. The yield variations in the substitution reactions are consistent with a more rapid relaxation of H atoms into positions favorable for successful bonding of the T atom. However, more work is needed to clarify the nature of the reaction mechanisms in both of the recoil substitution reactions.

The moderator isotope effect measured here is in the opposite direction from that discussed earlier[5] and is not consistent with a quasi-elastic atomic collision process (T vs. H or D in the respective fluoride). Furthermore, the magnitude of the average energy loss is much too large for molecular elastic collisions and confirms the earlier measurements of substantial energy loss by inelastic collision mechanisms.[14,24,33] Detailed quantitative analysis of the process of moderation by polyatomic molecules is not feasible, however, until a suitable value of α_{He} or some other standard has been established.

The Polymerization of Cyclopentadiene by Free Ions. Determination of the Propagation Rate Constant[1,2]

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The technique of radiation-induced ionic polymerization at low temperature has been used to determine the propagation rate constant, $k_p = 5.8 \times 10^{8\pm1} M^{-1} sec.^{-1}$, for the polymerization of cyclopentadiene by free ions at $-78°$. In this method, ammonia has been employed as a terminating agent to obtain the ratio of rate constants, k_r/k_p, for termination to propagation, while the value of k_r has been calculated from the Smoluchowski-Debye theory for encounter-controlled reactions. The significance of high k_p values for polymerization by free ions is discussed with reference to conventional ionic polymerization.

Introduction

Evidence has accumulated which indicates that under certain conditions, the radiation-induced polymerization of several monomers including isobutylene,[3] α-methylstyrene,[4] β-pinene,[5] styrene,[6-9] isobutyl vinyl ether,[10] and butadiene[11,12] is caused by ionic intermediates. Despite the attention devoted to this topic, little progress has been made in the elucidation of rate constants. In particular, no information has been available to allow any discrimination between the possible participation of free ions and/or ion pairs in these polymerizations. Some theoretical views[13-15] have been advanced, but a lack of precise knowledge has hampered any further clarification of this subject.

The present contribution deals with certain aspects of the radiation-induced polymerization of cyclopentadiene at $-78°$. We have previously reported[2,16] on the use of ammonia as a suitable ion scavenger and retarder of ionic polymerization. In this paper, results are presented on the molecular weights of the polymer formed in the presence of ammonia, and the Mayo-Overberger relation[17,18] is applied to obtain the ratio of rate constants for propagation to retardation. By employing tritiated ammonia, it has been possible to measure the concentration of amino groups in samples of soluble polymer. In addition, we report on the effects of temperature, dose rate, and other additives on this radiation-induced polymerization.

Experimental

Materials. Cyclopentadiene monomer was prepared by the thermal decomposition of the dimer 3a,4,7,7a-tetrahydro-4,7-methanoindene (Matheson Coleman and Bell, practical, 95%) in an 8-ft. Vigreux column under an atmosphere of nitrogen. After condensation, the monomer was collected in a receiving flask held at $-78°$. By vapor phase chromatography, the purity of the

(1) (a) This work was supported by the Atomic Energy Commission under Contract No. AT-(40-1)-2968; (b) based partially upon the Ph.D. dissertation of W. R. B. (University of Tennessee, 1963); (c) presented in part at Symposium on Radiation-Induced Polymerization, Division of Polymer Chemistry, 148th National Meeting of the American Chemical Society, Chicago, Ill., 1964.
(2) A preliminary communication has been published: M. A. Bonin, W. R. Busler, and F. Williams, *J. Am. Chem. Soc.*, **84**, 4355 (1962).
(3) (a) W. H. T. Davison, S. H. Pinner, and R. Worrall, *Proc. Roy. Soc.* (London), **A252**, 187 (1959); (b) E. Collinson, F. S. Dainton, and H. A. Gillis, *J. Phys. Chem.*, **63**, 909 (1959).
(4) J. V. F. Best, T. H. Bates, and F. Williams, *Trans. Faraday Soc.*, **58**, 192 (1962).
(5) T. H. Bates, J. V. F. Best, and F. Williams, *J. Chem. Soc.*, 1531 (1962).
(6) A. Chapiro and V. Stannett, *J. chim. phys.*, **56**, 830 (1959).
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(8) A. Charlesby and J. Morris, *Proc. Roy. Soc.* (London), **A273**, 378 (1963).
(9) S. Okamura, T. Higashimura, and S. Futami, *Intern. J. Appl. Radiation Isotopes*, **8**, 46 (1960).
(10) M. A. Bonin, M. L. Calvert, W. L. Miller, and F. Williams, *Polymer Letters*, **2**, 143 (1964).
(11) W. S. Anderson, *J. Phys. Chem.*, **63**, 765 (1959).
(12) R. L. Webb, "Proceedings of the International Symposium on Radiation-Induced Polymerization," Battelle Memorial Institute, 1962, A.E.C. Report TID-7643, p. 109.
(13) M. Magat, *Makromol. Chem.*, **35**, 159 (1960); *J. Polymer Sci.*, **48**, 379 (1960).
(14) F. S. Dainton, *Makromol. Chem.*, **35A**, 120 (1960).
(15) M. Szwarc, *ibid.*, **35A**, 123 (1960).
(16) W. R. Busler, D. H. Martin, and F. Williams, *Discussions Faraday Soc.*, **36**, 102 (1963).
(17) F. R. Mayo, *J. Am. Chem. Soc.*, **65**, 2324 (1943).
(18) C. G. Overberger, G. F. Endres, and A. Monaci, *ibid.*, **78**, 1969 (1956).

monomer exceeded 99%. Ammonia gas (Matheson Co., 99.99%) was obtained from a lecture bottle and dried over a sodium mirror in the vacuum system. Anthracene (Eastman reagent grade) was purified by sublimation before use. DPPH, 1,1-diphenyl-2-picrylhydrazyl (Eastman reagent grade), was used without purification. Oxygen was prepared in the vacuum line by the thermal decomposition of dry mercury(II) oxide (Baker analyzed reagent grade). Toluene and carbon tetrachloride (Baker analyzed reagent grade) were used as solvents for polycyclopentadiene. Silica gel (Davison PA-100, refrigeration grade) was activated at 250° for about 10 hr. and cooled in a closed container before use as a drying agent for cyclopentadiene.

Technique. Samples of cyclopentadiene for irradiation were prepared in ampoules or dilatometers by standard high-vacuum methods.[4,16] The monomer was normally dried by passage over activated silica gel, but to test the efficacy of this method, some runs were made in which the monomer was also left in contact with a mirror of metallic sodium on the vacuum manifold for several hours. Considerable care was taken to keep the cyclopentadiene at low temperatures (-40 to $-78°$) during all operations to minimize the spontaneous formation of dimer. Where ammonia was to be added to the monomer, a precise volume of the gas was measured under standard conditions before transfer. For the addition of oxygen, the sample was sealed off at a measured O_2 pressure above the solid monomer. In the case of solid additives (DPPH and anthracene), a known weight was first introduced into the sample tube, and, after evacuation, the cyclopentadiene was added by low temperature distillation.

The dilatometers were constructed from Pyrex glass with stems of precision capillary tubing (0.1250 ± 0.0002 in. i.d.). Dilatometer volumes (usually in the range of 10–20 ml.) were determined by prior calibration with water to a reference mark on the stem.

All samples were irradiated in a cobalt-60 γ-radiation source at the Oak Ridge National Laboratory. The dose rates in the various positions were determined with the Fricke dosimeter using the value[19] $G(Fe^{+2}$ oxidized) = 15.6 ions/100 e.v. The factor of 0.985 is used to convert dose rates in e.v. g.$^{-1}$ min.$^{-1}$ from the dosimeter solution to cyclopentadiene, this being the ratio of electrons per gram in cyclopentadiene to 0.4 M H_2SO_4. In most runs, the monomer sample was held at constant temperature inside a dewar vessel during irradiation. The majority of this work was carried out at $-78°$ using solid carbon dioxide–acetone as the coolant.

The polymerization was followed by measuring the degree of volume contraction. The dilatometer was periodically removed from the source and inserted into another large dewar flask containing a well-stirred slurry of trichlorethylene and solid CO_2 at $-78°$. After suitable mounting, the stem of the dilatometer could be viewed through an unsilvered window in the dewar, and the distance between the liquid meniscus and reference mark was measured with a cathetometer to ±0.1 mm.

Characterization of Polymer. The yield of polymer was determined gravimetrically. Usually, the weighed sample tube was cracked open and the entire contents

placed in a round-bottomed tube which could be attached to the vacuum system. The remaining monomer was distilled off rapidly *in vacuo* and the residual polymer determined. The nature of the polymer depended upon the concentration of ammonia present in the monomer and on the irradiation dose received (*vide infra*). In the absence of ammonia, a soft gel was formed at doses as low as 0.01 Mrad (6.2 × 10^{17} e.v. g.$^{-1}$), and complete conversion to a hard rubbery solid was effected after about 1 Mrad. With ammonia present, the gel point was only attained (if at all) at much higher doses, the exact value depending upon the initial amount of ammonia added. In appearance, the freshly isolated polymer from low conversion runs ($NH_3 < 10^{-3}$ M) was white and pliable, but it soon became yellow and brittle after standing in the atmosphere for a few hours.

The polymer from the irradiation of pure monomer always contained an insoluble gel fraction, even at the very lowest conversions ($\sim 1\%$). On the other hand, the polymer from several of the ammonia runs was completely soluble in toluene and intrinsic viscosity measurements were carried out on such solutions using an Ostwald viscometer. An antioxidant (0.1 wt. % β-naphthylamine) was added.

Infrared spectra were obtained for solutions of polymer in carbon tetrachloride and for polymer films cast on sodium chloride optical plate. N.m.r. spectra were also taken on carbon tetrachloride solutions, using a Varian A-60 spectrometer.

It was of some interest to determine whether ammonia was actually incorporated into the polymer during polymerization, presumably in the form of amino end groups. Experiments were carried out using a high concentration(0.2 M)of tritium-labeled ammonia with an activity of 7.02 mc./mole. The polymer was isolated, dissolved in toluene containing suitable additives (2,5-diphenyloxazole and 2,2'-p-phenylenebis(5-phenyloxazole)), and the activity counted[20] at $-18°$ with a Baird-Atomic Model 745 liquid scintillation counter.

Results

Polymerization Rates and Yields. A summary of our data for the polymerization of pure monomer at $-78°$ is shown in Table I. The average value of G $(-C_5H_6)$ from these measurements is 21,200 with a mean deviation of 3000 and a standard deviation of 3500. For the same system, Bates has reported[21] that $G-(C_5H_6) = 17,800$, and more recent work by the same author and his co-workers (private communication) gives a mean $G(-C_5H_6)$ of 21,100 with a standard deviation of 2800. Considering the lack of reproducibility which often attends the study of radiation-induced ionic polymerization, the measure of agreement between the two independent sets of data is highly satisfactory. Moreover, the relatively low standard deviation from the mean yield confirms the suitability of the system for a detailed quantitative investigation of the effects of additives. The constancy of $G(-C_5H_6)$ in Table I implies that the conversion is simply proportional to the dose, and this is confirmed by linear

(19) C. J. Hochanadel and J. A. Ghormley, *J. Chem. Phys.*, 21, 880 (1953).

(20) J. F. Eastham, H. L. Westbrook, and D. Gonzales, "Tritium in the Physical and Biological Sciences," Vol. I, International Atomic Energy Agency, Vienna, 1962, p. 203.

(21) T. H. Bates, *Nature*, 197, 1101 (1963):

Table I. Polymerization Yields for Cyclopentadiene at $-78°$

Sample code	Dose rate $\times 10^{-18}$, e.v. g.$^{-1}$ min.$^{-1}$	Dose $\times 10^{-18}$, e.v. g.$^{-1}$	Con-version, wt. %	$G(-C_5H_6)$, molecules/ 100 e.v.
A193	0.28	1.0	2.05	18,700
A194	0.28	1.0	2.06	18,700
A195	0.28	1.0	2.26	20,600
A177	0.28	1.0	1.70	15,500
A174	0.28	0.4	1.00	22,800
A166	0.28	1.0	2.57	23,400
A49	0.31	2.0	4.87	22,200
A119	0.29	2.2	4.07	16,900
A89	0.31	2.5	4.36	15,900
A26	0.32	10.0	25.5	23,200
A13	0.32	10.0	21.4	19,500
A205	0.27	1.0	2.86	26,100
A202	0.27	1.5	4.37	26,500
A207	0.27	1.0	2.68	24,400
A206	0.27	1.0	2.62	23,900

Table II. Effect of Temperature on the Radiation-Induced Polymerization of Cyclopentadiene[a]

Sample code	Temp., °C.	Dose $\times 10^{-18}$, e.v./g.	Con-version, wt. %	$G(-C_5H_6)$, molecules/ 100 e.v.
A193	-78	1.0	2.05	18,700
A205	-78	1.0	2.86	26,100
A206	-49	1.0	2.62	23,900
A194	-48	1.0	2.06	18,800
A195	-30	1.0	2.26	20,600
A207	-29	1.0	2.68	24,400
A197	0	1.0	0.70	6,400
A204	0	1.0	0.82	7,500
A203	22	1.0	0.54	4,900

[a] Dose rate $= 0.27 \times 10^{18}$ e.v. g.$^{-1}$ min.$^{-1}$.

kinetic plots of volume contraction against dose for individual runs on the pure monomer.[16]

Apart from the work already cited, two other reports on cyclopentadiene polymerization by irradiation have come to our attention. First, a patent[22] has disclosed that the irradiation of cyclopentadiene at 0° or lower for a total dose of 16 Mrads (1.0 $\times$ 10^{21} e.v./g.) gives a product which can be diluted with cyclohexane to form a polymer "base." In our experience, even 1 Mrad at $-78°$ converts the monomer to a hard impervious rubber. At 0°, we find that the conversion per unit of dose is much less (*vide infra*), but at this temperature the results are probably seriously affected by the spontaneous formation of dimer which may act as a polymerization retarder (compare ref. 3a). Secondly, through the kindness of Dr. K. Hayashi, we have been able to gain access to the work of Hayashi, Hamada, and Okamura.[23] These authors report conversions of about 2% per Mrad for cyclopentadiene at $-78°$, which is about a factor of 50 less than that obtained in our work. The cause of this large discrepancy is uncertain but we suggest that it is probably related to the different methods used to pretreat the monomer before irradiation. Variations in the order of magnitude of radiation-induced polymerization yields as recorded by different workers have also been noted for α-methylstyrene.[24] In the present case, it should also be remarked that the pretreatment methods used by Bates[21] and ourselves are virtually identical.

Because the radiation-induced polymerization of α-methylstyrene and β-pinene has been shown[4,5] to be very sensitive to traces of water, we wished to know if the polymerization yield for cyclopentadiene could be increased by even more stringent drying of the monomer. In three experiments, the monomer was given an additional treatment on sodium mirrors, but the average yield for these runs was $G(-C_5H_6) = 19,000$, which lies within the standard deviation of the other results.

Turning to the effect of temperature on the polymerization yield, the results in Table II show little variation in $G(-C_5H_6)$ below $-30°$, but above this

temperature there is rather an abrupt decrease in the conversion yield per unit dose. Clearly, the temperature dependence of the polymerization rate cannot be represented by Arrhenius parameters over the entire range studied. Bates[21] has also noted that the polymerization yield is lower and less reproducible at 0°. Hayashi, *et al.*,[23] report an activation energy of -3.1 kcal./mole for the polymerization in the liquid state. However, it is likely that the results above $-30°$ are affected by the spontaneous dimerization of cyclopentadiene in the system. From the data of Wassermann,[25] the second-order rate constants for dimerization at 0 and $-78°$ in pure cyclopentadiene are calculated to be 6.9 $\times$ 10^{-8} and 4.5 $\times$ 10^{-13} M^{-1} sec.$^{-1}$, respectively. Hence the corresponding rates of dicyclopentadiene formation are 5.0 $\times$ 10^{-6} M sec.$^{-1}$ at 0° and 3.9 $\times$ 10^{-11} M sec.$^{-1}$ at $-78°$. In the interval of about 4 min. during our irradiations (Table II), a dimer concentration of *ca.* 1.2 $\times$ 10^{-3} M would therefore be attained at 0°, whereas for monomer held at $-78°$, the concentration would be considerably less. Since it has been shown[3a] that added 10^{-1} M diisobutylene depresses the conversion yield in the radiation-induced polymerization of isobutylene by a factor of 45, it is probable that appreciable concentrations ($\sim 10^{-3}$ M) of dicyclopentadiene can exert a significant effect in the present system. This explanation derives further support from our finding that samples of cyclopentadiene left at room temperature for periods of several hours gave very low polymerization yields on subsequent irradiation at $-78°$.

The results of a typical dilatometric experiment are reproduced in Figure 1 to illustrate the effect of dose rate on the polymerization of the pure monomer. For purposes of calibration, it has been established from eleven determinations that a volume contraction of 1% corresponds to the conversion of 5.74% ($\pm 0.26\%$) of cyclopentadiene monomer to polymer. It is seen from Figure 1 that the change in dose rate is accompanied by only a very slight change of slope in the linear plots of conversion against dose, from which it may be deduced that the rate of polymerization is proportional to the 1.07 power of the dose rate. In other experiments of this type, the dose rate power dependence has been found to be 1.0 $\pm$ 0.1. This is a fairly common result in studies of radiation-induced ionic polymerizations,[3-8] although a recent exception to this trend should be noted.[10]

(22) British Patent 831,139; *Chem. Abstr.*, **55**, 13906g (1961).
(23) K. Hayashi, H. Hamada, and S. Okamura, *Ann. Rept. Japan. Assoc. Radiation Res.*, **2**, 101 (1960).
(24) T. H. Bates, J. V. F. Best, and F. Williams, *Nature*, **188**, 469 (1960).
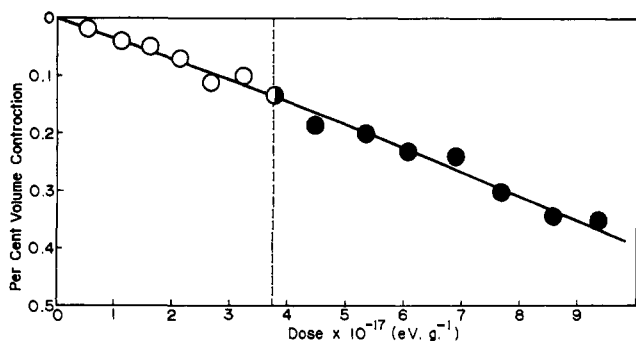(25) G. A. Benford, H. Kaufmann, B. S. Khambata, and A. Wassermann, *J. Chem. Soc.*, 381 (1939).

Figure 1. Effect of dose rate on rate of polymerization of cyclopentadiene at $-78°$: O, 0.27×10^{17} e.v. g.$^{-1}$ min.$^{-1}$; ●, 2.8×10^{17} e.v. g.$^{-1}$ min.$^{-1}$.

During the course of this work, the diameter of the cylindrical irradiation ampoules has ranged between 15 and 45 mm., while the amount of monomer per sample tube has been varied from 5 to 100 ml. No discernible change in $G(-C_5H_6)$ for pure monomer has been detected as a result of these variations in the size of sample container.[26]

Effect of Additives. The effect of ammonia concentration on the *initial* rate of polymerization has been described in a previous paper.[16] The data of Table III refer to a set of measurements at constant dose where the degree of conversion to polymer was measured for differing concentrations of added ammonia.

Table III. Dependence of Polymer Yield at $-78°$ on Ammonia Concentration

Sample code	Dose rate × 10^{-18}, e.v. g.$^{-1}$ min.$^{-1}$	Dose × 10^{-20} e.v./g.	[NH$_3$] × 10^4, moles/l.	Conversion, wt. %	$G(-C_5H_6)$, molecules/ 100 e.v.
A125	1.85	1.0	1.57	5.86	534
A122	1.85	1.0	1.96	4.20	383
A120	1.85	1.0	2.47	3.68	335
A103	1.93	1.0	7.27	2.61	238
A105	1.93	1.0	22.8	1.52	139
A190	1.77	1.0	200.0	0.57	52

In view of the sensitivity of this polymerization to the presence of ammonia and amines, it was of some interest to examine the effect of other additives. Table IV shows the results of a series of experiments with anthracene, a relatively weak base[27] compared to ammonia. A comparison of the action of DPPH and oxygen, two typical free-radical scavengers, is furnished by the data of Table V. It is clear that ammonia and trimethylamine are the most effective polymerization retarders among this group of additives.

Two experiments have been carried out with ammonia-d_3. Following irradiation, the volatile gas at $-196°$ was measured and then analyzed with a mass spectrometer. The results in Table VI show that the

(26) The reproducibility of the yield for different ampoule surface area/volume ratios indicates that heterogeneous effects are unimportant in this system. In this connection, it has been shown (F. L. Dalton and K. Hayakawa, *Polymer*, **4**, 285 (1963)) that added solids do not enhance the radiation-induced polymerization of α-methylstyrene which is known to proceed by an ionic mechanism.[4]

(27) E. L. Mackor, A. Hofstra, and J. H. van der Waals, *Trans. Faraday Soc.*, **54**, 66 (1958).

Table IV. Polymer Yields for Solutions of Anthracene in Cyclopentadiene Irradiated at $-78°$[a]

Sample code	[Anthracene] × 10^3, moles/l.	Dose × 10^{-18}, e.v./g.	Conversion, wt. %	$G(-C_5H_6)$, molecules/ 100 e.v.
A180	1.0	1.0	0.60	5470
A183	1.0	1.5	0.75	4560
A181	1.0	5.0	2.61	4760
A179	1.0	10.0	5.05	4600
A178	1.0	15.0	7.66	4650
A184	9.4	12.0	3.10	2350

[a] Dose rate = 0.28×10^{18} e.v. g.$^{-1}$ min.$^{-1}$.

Table V. Effect of Additives on Polymerization Yields[a] at $-78°$

Sample code	Additive	Concn., moles/l.	Dose × 10^{-18}, e.v./g.	Conversion, wt. %	$G(-C_5H_6)$, molecules/ 100 e.v.
A195	None	...	1.00	2.26	20,600
A160	DPPH	5.0×10^{-3}	1.41	1.26	8,140
A161	DPPH	5.0×10^{-3}	2.83	2.69	8,660
A162	O$_2$	1.8×10^{-3}	2.83	1.50	4,830
A163	O$_2$	1.7×10^{-3}	1.41	0.89	5,750
A183	Anthracene	1.0×10^{-3}	1.50	0.75	4,560
A137	(CH$_3$)$_3$N	0.9×10^{-3}	25.0	1.24	450
A140	NH$_3$	0.9×10^{-3}	50.0	1.38	252

[a] Dose rate = 0.28×10^{18} e.v. g.$^{-1}$ min.$^{-1}$.

G yield of hydrogen from cyclopentadiene is low (0.17) and that the amount of HD formed in the presence of ND$_3$ is negligible. Corresponding concentrations of ND$_3$ in cyclohexane[16] produced about 5% HD with a total G(hydrogen) yield of 5.6. It must be concluded that any deuterium atoms produced in the cyclopentadiene-ND$_3$ system at $-78°$ undergo addition rather than abstraction reactions.

Properties of Polymers. The nature of the polymer formed by the irradiation of cyclopentadiene at $-78°$ is directly related to the concentration of ammonia present during irradiation and to the dose received by the sample. Some typical results which indicate the general trends are summarized in Table VII. It can be seen that the proper selection of ammonia concentration and irradiation dose leads to the formation of soluble polymers. In such cases, the molecular weights of the polymers have been determined from intrinsic viscosity measurements according to the relation, $[\eta] = K\bar{M}_v{}^a$. The constants $K = 1.5 \times 10^{-4}$ and $a = 0.74$ have been used since these values refer to polyisoprene,[28] a polymer whose viscosity behavior in solution might reasonably be expected to resemble that of polycyclopentadiene. In Table VIII, the results have been calculated on the assumption that $\bar{M}_v = \bar{M}_n$ whereas for a most probable distribution, $\bar{M}_v/\bar{M}_n$ is usually taken as 1.8. However, this uncertainty does not affect the relative $\overline{DP}$ values, which increase progressively as the ammonia concentration is lowered. This behavior is fully consistent with the role of ammonia as a chain terminator, and the quantitative aspects are discussed later.

The results obtained with tritium-labeled ammonia can be used to calculate an apparent molecular weight,

(28) H. Brady, M. Ladacki, R. Milkovitch, and M. Szwarc, *J. Polymer Sci.*, **25**, 221 (1957).

Table VI. Yields and Isotopic Composition of Hydrogen from the Irradiation of Cyclopentadiene + Ammonia-d_3 Solutions at $-78°$

Sample code	[ND$_3$] concn., moles/l.	Dose rate $\times 10^{-18}$, e.v. g.$^{-1}$ min.$^{-1}$	Dose $\times 10^{-20}$, e.v./g.	H$_2$, % (total)	G(H$_2$); molecules/ 100 e.v.	Isotopic analysis, %		
						H$_2$	HD	D$_2$
E10	1.8×10^{-2}	1.77	1.0	98.6	0.18	99.76	0.20	0.04
E11	2.2×10^{-2}	0.28	9.97	99.9	0.16	99.81	0.19	0.00

Table VII. Dependence of Polymer Solubility on Irradiation Conditions

Sample code	[NH$_3$] $\times 10^3$, moles/l.	Dose $\times 10^{-21}$, e.v./g.	Conversion, wt. %	Remarks
A202	None	0.0015	4.37	Insoluble gel swells in toluene
A8	None	0.05	ca. 100	Hard rubber
A79	3.5	1.0	13.7	Soluble in CCl$_4$
A80	3.5	3.0	45.2	Insoluble in CCl$_4$
A81	3.5	5.0	50	Hard rubber
A210	160.0	1.2	1.65	Soluble in toluene

p.p.m. downfield relative to tetramethylsilane (δ 0). It can be seen that of the three peaks in the low-field region characteristic of olefinic protons, the one at δ 5.61 p.p.m. is much the most intense and the area under this peak represents at least 80% of the total. The minor peaks are located at δ-values of 5.41 and 5.89 p.p.m. In the high-field region, three broad absorption bands are evident with maxima at 1.6, 2.1, and 2.65 p.p.m. The total area under the olefinic protons is exactly half of the integrated area over the high-field absorption region extending from 3.0 to

Table VIII. Molecular Weights of Soluble Polycyclopentadiene Polymers

Sample code	[NH$_3$] $\times 10^4$, moles/l.	Dose $\times 10^{-20}$, e.v./g.	G(−C$_5$H$_6$), molecules/ 100 e.v.	$[\eta]$, dl./g.	$\bar{M}_v$	$\overline{DP}$	G(−C$_5$H$_6$)/ $\overline{DP}$
A176	25.0	3.0	91	0.210	17,800	269	0.34
A200	17.9	2.4	106	0.315	30,900	468	0.23
A199	12.9	2.0	112	0.385	40,400	611	0.18
A173	7.5	1.9	164	0.430	47,100	712	0.23
A172	2.5	1.3	340	0.790	107,000	1,620	0.21
A175	2.3	0.80	300	1.02	151,000	2,280	0.13
A174[a]	None	0.004	22,800	2.76	581,000	8,800	

[a] Refers only to the sol fraction of the polymer.

Table IX. Incorporation of Tritium into Polymer Formed in the Presence of Labeled Ammonia

Sample code	Dose $\times 10^{-20}$, e.v./g.	[NH$_3$], moles/l.	$A_0 \times 10^{-10}$, d.p.m./mole	$A_e \times 10^{-6}$, d.p.m./g.	$\bar{M}_a$	G(−C$_5$H$_6$)	G(RNH$_2$)
A208	7.6	0.18	1.56	2.55	4080	20	0.32
A210	12.0	0.16	1.56	1.45	7170	19	0.18
A211	9.6	0.19	1.56	4.23	2460	14	0.38

$\bar{M}_a$, for the polymer on the assumption that each polymer molecule is formed with a terminal R–NH$_2$ group. If A_0 is the molar activity of the labeled ammonia, and A_e represents the specific activity per gram of polymer, it follows that $M_a = \frac{2}{3}(A_0/A_e)$, where the factor of $\frac{2}{3}$ is a statistical correction to allow for the loss of activity in the transformation from NH$_3$ to R–NH$_2$. Rather large ammonia concentrations were used in these experiments in order to have optimum conditions for the detection of the end groups. Because of these circumstances, the precision of the G(−C$_5$H$_6$) values is rather low, and the results of Table IX should be regarded only as semiquantitative. However, it is evident that G(RNH$_2$) is in general agreement with the yield of initiators, G(−C$_5$H$_6$)/$\overline{DP}$, given in Table VIII, which implies that the termination reaction is primarily of the Lewis acid–base type.

Proton Magnetic Resonance and Infrared Spectra. In Figure 2, the proton magnetic resonance spectrum of a polymer sample dissolved in carbon tetrachloride is displayed. Chemical shifts are given as δ values in

1.0 p.p.m., and this result verifies that the repeating unit –C$_5$H$_6$– in the polymer contains two olefinic protons. Comparisons with the spectra[29,30] of model ring compounds lead to the tentative assignments of the poorly resolved bands at 1.6, 2.1, and 2.65 p.p.m. to those of nonallylic >CH$_2$, allylic >CH$_2$, and allylic ≫CH protons, respectively. If this is correct, then the relative areas of these bands suggest that 1,2 addition polymerization leading to allylic >CH$_2$ is somewhat less frequent than 1,4 addition. It is also interesting that the two types of olefinic protons in dicyclopentadiene have been observed[30] at 5.4 (cyclopentene ring) and 5.87 p.p.m. (norbornene ring), which correspond almost exactly to the positions of the two minor peaks for the polymer spectrum. On the other hand, the position of the main olefinic proton in the polymer is very close to that observed for the olefinic protons in

(29) NMR Spectra Catalog, Varian Associates, Palo Alto, Calif., 1962.

(30) G. Van Dyke Tiers, Characteristic NMR Spectral Positions for Hydrogen in Organic Structures, Minnesota Mining and Manufacturing Co., St. Paul 19, Minn., 1959, Table II, pp. 7 and 8.
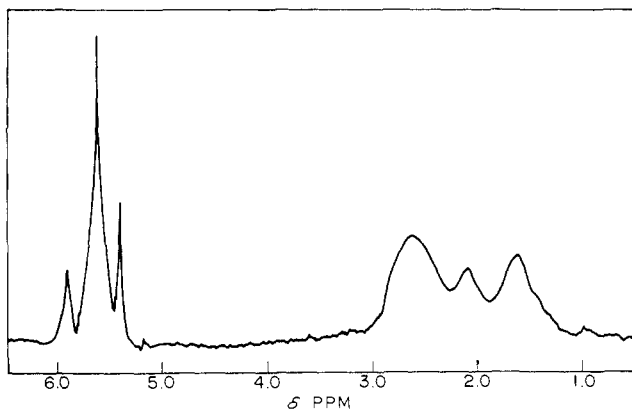
Figure 2. N.m.r. spectrum of polymer in carbon tetrachloride.

cyclohexene (5.57 p.p.m.)[30] and other monocyclic olefins.

The infrared spectra of polymers formed in the presence and absence of ammonia are very similar, and show the expected bands at 6.1 (sharp) and 13.1–14.8 μ (very broad) characteristic of cis-olefin groups. In addition to these and the C–H bands at 3.2 (sharp) and 3.4 μ (broad), other absorption bands are particularly pronounced at 6.9 (sharp single peak) and 7.35 μ (doublet), and in the 10.6–11.0-μ region.

Discussion

A consequence of retardation by ammonia in this system is that the molecular weight of the polymer should be governed by the ammonia concentration if chain transfer to monomer is infrequent. The data in Table VIII bear out this expectation, for the molecular weights decrease monotonically as a function of the ammonia concentration. The high molecular weight of the polymer formed from pure cyclopentadiene explains the efficiency with which this polymer cross-links to form gel networks at very low conversion, and allows the additional inference that chain transfer to monomer is relatively unimportant in determining the molecular weight when ammonia is present.

The last column of Table VIII gives the calculated values for the quotient $G(-C_5H_6)/\overline{DP}$, which represents the total number of ions, per 100 e.v., growing to polymer. The mean value is 0.22 with a standard deviation of 0.07. It is of considerable interest that this initiation yield is not far different from the G yields of free ions that have been determined by physical measurements on the conductivity of radiolytic ions in saturated hydrocarbons.[31,32] By such techniques, Allen and Hummel[31] have obtained $G = 0.09 \pm 0.04$ in n-hexane, while Freeman[32] has reported $G = ca.$ 0.2 for cyclohexane. In addition, a chemical method based on the use of ammonia-d_3 as a proton scavenger for radiolytic ions in cyclohexane[33] has given G(free ions) $= 0.08$.

The standard method of determining the reactivity of a terminating agent in polymerization is based upon the use of the Mayo–Overberger relation,[17,18] which predicts that the reciprocal of the number-average degree of polymerization, $1/\overline{DP}$, should be a linear function of

(31) A. O. Allen and A. Hummel, Discussions Faraday Soc., 36, 95 (1963).
(32) G. R. Freeman, J. Chem. Phys., 39, 988 (1963).
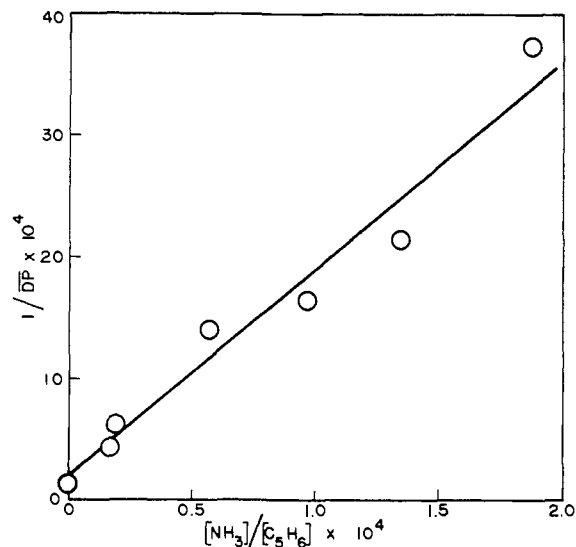(33) F. Williams, J. Am. Chem. Soc., 86, 3954 (1964).

Figure 3. Dependence of degree of polymerization on ammonia concentration.

the molar concentration ratio of the terminator (retarder) to monomer, [R]/[M], according to the equation

$$\frac{1}{\overline{DP}} = \frac{1}{\overline{DP_0}} + \frac{k_r}{k_p}\frac{[R]}{[M]} \tag{1}$$

where $\overline{DP_0}$ is the number-average degree of polymerization in the absence of terminator. The slope of the plot of $1/\overline{DP}$ against [R]/[M] gives the ratio of rate constants k_r/k_p, where k_r and k_p are the rate constants for termination (by ammonia in this system) and propagation, respectively. Using this approach, we obtain $k_r/k_p = 16.8$ from the slope of the appropriate plot in Figure 3. In this instance, the ammonia concentrations refer to initial values, so an error is introduced if the retarder concentration is substantially depleted during the run. From earlier work,[16] we know that the rate of polymerization increases on prolonged irradiation at low ammonia concentrations, but it is not entirely clear whether this is due to a depletion of retarder, a viscosity effect on diffusion-controlled termination, or a combination of both. In any event, the operation of this nonlinear effect has been minimized in this work by using small irradiation doses to form polymer at low ammonia concentrations.

In a previous paper,[16] it has been shown that the initial yield of monomer disappearance, $G(-C_5H_6)$, as a function of ammonia concentration is compounded of two terms according to the relation

$$G(-C_5H_6) = G_x\frac{k_p[C_5H_6]}{k_r[NH_3]} + G_c(-C_5H_6) \tag{2}$$

where $G_c(-C_5H_6)$ has the form $A[C_5H_6]/(B[NH_3] + C)$. The first term of relation 2 represents the yield due to initiators which are terminated only by ammonia over the whole range of additive concentration employed, whereas the second term, $G_c(-C_5H_6)$, is only substantially lowered by ammonia concentrations exceeding about 10^{-3} M. In the light of recent work with ammonia-d_3 as a proton scavenger in cyclohexane,[33] it is apparent that ammonia concentrations exceeding 10^{-3} M can react not only with free ions, but also begin to compete with the geminate ionic

recombination processes. Therefore, we identify the first term of relation 2 as the contribution to the $G(-C_5H_6)$ yield from the polymerization by free ions, whereas the second term is taken to represent the propagation by ions which undergo geminate recombination in times less than about 10^{-7} sec. In the absence of ammonia, the term $G_c-(C_5H_6)$ accounts for less than 1% of the total yield so that almost all the polymerization is then due to free ions. On the other hand, at 10^{-3} M ammonia concentration, the free ion polymerization is considerably repressed and there is a comparable yield due to the nonseparated ion pairs.

A referee has pointed out that the data of Table III show a dependence of conversion on the $-1/2$ power of ammonia concentration. By including the results of Table IX, we confirm that this dependence holds accurately for the concentration range 10^{-3} M < [NH_3] < 10^{-1} M, where it can be shown that the second term of eq. 2 predominates (e.g., using the previous determination[16] of $G_x k_p/k_r = 3.1 \times 10^{-3}$, the first term of eq. 2 contributes only 2.0 at [NH_3] = 0.02 M to the observed $G(-C_5H_6)$ value of 52 given in Table III). To the extent that the first term of eq. 2 may be neglected, $G(-C_5H_6)$ can be represented by the summation

$$\sum_g G_g \frac{k_p[C_5H_6]}{k_r[NH_3] + k_g}$$

where G_g is the specific yield of ions undergoing geminate recombination in a mean time $1/k_g$. Now, in a study of the cyclohexane–ND_3 system,[33] it has been found that in the same concentration region (10^{-3} to 10^{-1} M) where ion scavenging by ammonia (ND_3) competes with geminate recombination the yield of scavengeable ions G_s represented by

$$G_s = \sum_g G_g \frac{k_r[ND_3]}{k_r[ND_3] + k_g}$$

obeys the empirical relation $G_s = K[ND_3]^{1/2}$ and the constant K is evaluated to be 2.5 ions/100 e.v. $M^{-1/2}$. Assuming that $k_r[NH_3] \sim k_r[ND_3]$ and that the unknown ion lifetime distribution represented by the parameters G_g and k_g is identical in the two systems, we obtain the relation

$$G(-C_5H_6) = K \frac{k_p[C_5H_6]}{k_r[NH_3]^{1/2}} \qquad (2a)$$

which fits the observed dependence at high ammonia concentration. The linear plot of $G(-C_5H_6)$ against [NH_3]$^{-1/2}$ gives a slope of 6.5 molecules/100 e.v. $M^{1/2}$, so that the ratio k_r/k_p is deduced to be ~ 5. Since the treatment is empirical and depends on related data from another system,[33] it is felt that this value of k_r/k_p is not as reliable as the independent determination of $k_r/k_p = 16.8$ from the Mayo–Overberger plot. The most important point is the striking consistency in the kinetics of geminate ion recombination in the two independent systems.

The term $G_x k_p/k_r$ in relation 2 has been evaluated from our previous data on initial rates of polymerization[16] and is equal to 3.1×10^{-3} molecule/100 e.v. Combining this result with the value $k_r/k_p = 16.8$ obtained from the Mayo–Overberger plot in Figure 3, we obtain $G_x = 0.05$ ion/100 e.v. This latter value is lower

than the total yield of polymerization initiators $G_i = 0.22$ measured by the quotient $G(-C_5H_6)/\overline{DP}$ in Table VIII. The most obvious reason for this discrepancy is that G_x refers only to free ions, whereas the total yield G_i also includes the contribution of some geminate species with a relatively long natural lifetime (ca. 10^{-7} sec.). In view of the fact that the kinetic data reflect the complication due to two types of ions, it is remarkable that the Mayo–Overberger relation works so well in this instance, since this relation is based on a kinetically homogeneous group of ions undergoing simple competition between propagation and termination.

In order to put the propagation rate constant, k_p, on an absolute scale, we need to know the magnitude of k_r for the reaction of the propagating ion with ammonia. Now the *intrinsic* reaction rate constant for the reaction of a positive ion with the unshared electron pair of the ammonia molecule is likely to be very large indeed, so the calculation reduces to one of estimating the diffusion-controlled rate constant for an ion–dipole interaction. Following the Smoluchowski–Debye theory,[34,35] we have the relation

$$k_r = f \frac{2kT}{3\eta}\left(2 + \frac{\rho_1}{\rho_2} + \frac{\rho_2}{\rho_1}\right) \qquad (3)$$

where k is the Boltzmann constant, T is the absolute temperature, η is the viscosity of cyclopentadiene, ρ_1 and ρ_2 are the "hard-sphere" *radii* of the interacting particles, and f is a correction factor to account for ion–dipole interaction. To a first approximation, f is $\sigma/(\rho_1 + \rho_2)$, where σ is given in the present case by the expression

$$\sigma^2 = \bar{\mu}e/\epsilon kT \qquad (4)$$

such that the potential energy of the ion–dipole interaction at a separation distance σ is equal and opposite to kT. In eq. 4, $\bar{\mu}$ is the average dipole moment in the direction of the field F, e is the charge of a univalent ion, and ϵ is the dielectric constant. According to the Langevin theorem[36]

$$\bar{\mu} = \mu(\coth \chi - 1/\chi) \qquad (5)$$

where $\chi = \mu F/kT$. Since F at σ is $e/\epsilon\sigma^2$, χ reduces to $\mu/\bar{\mu}$ and is given by the equation

$$2/\chi = \coth \chi \qquad (6)$$

From a numerical solution of eq. 6, $\chi = 1.91$, so $\sigma = (\mu e/1.9\epsilon kT)^{1/2}$. Substitution of $\mu = 1.44 \times 10^{-18}$ e.s.u. cm. for the dipole moment of ammonia and $\epsilon = 2.0$ for the dielectric constant of cyclopentadiene together with appropriate values for fundamental constants leads to $\sigma = 8.2$ Å. at $T = 195°K$. If the locus of the positively charged center in the growing molecule is considered to be confined to the terminal cyclopentadiene unit, then the effective radius, ρ_1, of the positive ion is 3.1 Å. as calculated from the molar volume of cyclopentadiene; taking the radius, ρ_2, of ammonia to be equivalent to the N–H bond length of 1 Å., $\rho_1 + \rho_2 = 4.1$ Å., and hence $f = 2.0$. The viscosity, η, of cyclopentadiene at 195°K. is 1.2 cp. as

(34) M. von Smoluchowski, *Z. physik. Chem.*, **92**, 129 (1917).
(35) P. Debye, *Trans. Electrochem. Soc.*, **82**, 265 (1942).
(36) R. J. W. Le Fevre, "Dipole Moments," Methuen and Co., Ltd., London, 1948, p. 6.

determined by extrapolation from our measurements at higher temperatures. The calculation of k_r according to eq. 3 can now be completed and leads to the value of 1.6×10^{-11} cm.^{3} sec.$^{-1}$ or 9.7×10^9 M^{-1} sec.$^{-1}$. On the basis of existing data for proton-transfer reactions, we previously assumed[16] k_r to be of the order of 10^9 M^{-1} sec.$^{-1}$. In the ensuing calculations of this paper, we shall use $k_r = 9.7 \times 10^9$ M^{-1} sec.$^{-1}$ as the yardstick, but it must be borne in mind that the overall uncertainty is about a factor of ten.

Our results in Tables III, IV, and V show that ammonia is a much more effective terminator than DPPH, oxygen, or anthracene. Oxygen and DPPH have often been used as "free-radical scavengers" in radiation chemistry, but it is now clear that the use of these highly reactive paramagnetic molecules often involves considerable side complications.[37] The results with anthracene are of special interest because this compound has been used as a terminating agent in the conventional cationic polymerization of styrene.[38] A comparison of the data in Table V suggests that ammonia (k_r/k_p = 16.8) is at least a factor of about 20 more efficient than anthracene as a terminator, so this would imply a k_r/k_p value for anthracene of less than unity for cyclopentadiene polymerization. It is interesting that Overberger and Newton[38] obtained k_r/k_p = 0.44 for the terminating efficiency of anthracene in the stannic chloride polymerization of styrene. The lower terminating efficiency of anthracene relative to ammonia is readily explained as a consequence of the need for π-electron delocalization in the former for electrophilic substitution to proceed.

The previous data for (k_r/k_p) and k_r in the case of ammonia lead to a k_p value of $5.8 \times 10^{8 \pm 1}$ M^{-1} sec.$^{-1}$ for the absolute propagation rate constant of cyclopentadiene polymerization at $-78°$. Before discussing the significance of this result in relation to other polymerization work, it is appropriate to marshal the evidence in support of the role of ions and especially for the contribution of free ions to the radiation-induced polymerization of pure cyclopentadiene. The qualitative arguments rest on the following points: (1) that the polymerization of cyclopentadiene is known to be readily initiated by conventional cationic catalysis whereas free radical polymerization is less favorable[39]; (2) that the radiation-induced polymerization occurs at low temperature and involves little or no activation energy; and (3) that the radiation-induced polymerization is strongly retarded by ammonia and the amines whereas typical free-radical scavengers are much less efficient. Turning to the quantitative aspects, it has already been pointed out that the yield of initiators is comparable to the yield of free ions as determined in saturated hydrocarbons by other methods. The final argument rests on a calculation of the lifetimes of free ions. From the results of Allen and Hummel,[31] the recombination rate constant, k_2, for ions in n-hexane is 1.0×10^{12} M^{-1} sec.$^{-1}$. The mean lifetime of a free ion with respect to charge recombination is given by $\tau = (1/k_2 R_i)^{1/2}$, where R_i is the rate of initiation. For a dose rate of 4.2×10^{15} e.v. ml.$^{-1}$ sec.$^{-1}$ (Table I),

and taking G_x (free ions) = 0.05, $\tau = 1.7 \times 10^{-2}$ sec. For purposes of comparison, the mean lifetime of a propagating ion during growth in the pure monomer is given by

$$\tau_p = G_0(-C_5H_6)/G_x k_p[C_5H_6] \qquad (7)$$

Using the value $G_0(-C_5H_6)$ = 21,200 for pure cyclopentadiene and the previous values for G_x and k_p, τ_p is evaluated to be 0.5×10^{-4} sec. Although this is less than the free-ion lifetime τ, it is considerably greater than the lifetime of ions undergoing geminate recombination[33] in less than 10^{-7} sec. Now the difference between τ and τ_p is not symptomatic of a fundamental inconsistency but rather mirrors the fact that even in the polymerization of pure cyclopentadiene, termination must be due to impurities which need only be present in concentration [S] such that $\Sigma k_s[S]$ = $(1/\tau_p)$ sec.$^{-1}$. In other words, an impurity scavenger with a rate constant k_s equal to k_p could account for the termination if present at a concentration [S] as low as 3.4×10^{-5} M. Confirmation of the role of impurity termination comes from the fact that the polymerization rate for the pure monomer is independent of dose rate. According to the free-ion theory, $\tau \geqslant \tau_p$, so in the limit of no impurity termination, the ultimate yield of monomer disappearance is predicted by the expression

$$G_0(-\text{monomer}) = \tau G_x k_p[C_5H_6] \qquad (8)$$

and the rate of polymerization would then depend on the 0.5 power of the dose rate. Thus $G_0(-\text{monomer})$ values of the order of 10^6 could presumably be attained with rigorously pure monomer under the usual irradiation conditions.

The value of k_p (5.8×10^8 M^{-1} sec.$^{-1}$) obtained in this work invites more than casual interest. Despite the fact that carbonium ions are among the most important intermediates in organic chemistry, there is little or no information available concerning the rate constants for the "fast" step where the carbonium ion is itself reacting. A few previous attempts[40,41] have been made to measure rate constants for propagation in cationic polymerization. Hayes and Pepper[40] have reported a value of 7.6 M^{-1} sec.$^{-1}$ for the polymerization of styrene by sulfuric acid in 1,2-dichloroethane, while Okamura and his co-workers[41] have obtained k_p values in the range between 10 and 20 M^{-1} sec.$^{-1}$ for the polymerization of p-methoxystyrene catalyzed by iodine in ethylene chloride. We believe that no comparison is possible between these determinations and our own, since the conditions are so entirely different. However, it is difficult to believe that the *intrinsic* reactivity of carbonium ions in polymerization can differ by a factor of 10^7. In conventional cationic polymerization, the propagation step is often presumed to involve a relatively stable ion pair, and it is difficult, if not impossible, to estimate the effect of the proximity of the gegenion, solvation conditions, etc., on the facility of the propagation reaction in such a case. As a further complication, there is much evidence[42,43]

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to support Veselý's statement[44] that "the reaction of chain growth proceeds with the participation of free ions and not ionic pairs, as is postulated by many authors." At least, it is probably fair to say that the conclusions arising out of kinetic investigations on conventional ionic polymerization are equivocal on this question.[45] However, there are at least two cases where the results appear to suggest that the propagation reaction is extremely fast when a *free* (or partially free) ion is involved. First, the work of Kennedy and Thomas[46] on the cationic polymerization of isobutene at $-78°$ led them to suggest that under certain conditions, the growth of the chain could take place by a diffusion-controlled mechanism with a time for single monomer addition $(1/k_p[M])$ of about 8×10^{-11} sec. Since $[M]$ was about 1.5 M in these experiments, this would indicate a value of $k_p \sim 8 \times 10^9$ M^{-1} sec.$^{-1}$. It should be added that the authors[46] expressed the view that the reaction is probably not quite as rapid as their calculation would indicate. The second example comes from the recent work of Szwarc and his co-workers[47] on the anionic polymerization of styrene in tetrahydrofuran. These authors have shown that the propagation

rate constant for the free anion is 6.5×10^4 M^{-1} sec.$^{-1}$, whereas the corresponding value for the ion pair lies in the range between 120 and 200 M^{-1} sec.$^{-1}$, depending on the alkali metal counterion. Thus, since it is quite probable that many previous kinetic results reflect composite behavior due to free ions and ion pairs, the high reactivity of the free ion has not been fully realized because the concentration of free ions is generally very small by comparison with ion pairs under the usual polymerization conditions. It is clear that more work is required to resolve the position.

In conclusion, the high value for k_p obtained in this investigation appears to support Dainton's general contention[48] that propagation by unhindered cations is considerably faster than by free radicals. Although our results on the temperature dependence are not entirely unambiguous, the constant rate between -78 and $-30°$ would seem to imply that the activation energy for propagation cannot exceed that for a possible diffusion-controlled termination step, *viz.*, *ca.* 2 kcal./ mole.

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Electron Spin Resonance of
α- and β-Cobalt Phthalocyanine[1a]

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The magnetic properties of α- and β-cobalt phthalocyanine polymorphs diluted in metal-free, zinc, and nickel phthalocyanine were investigated by e.s.r. The spectra of the two complexes reveal the difference in their polymorphic structures. The Hamiltonian parameters, g-factors and hyperfine splitting constants, determined from polycrystalline samples are compared with single crystal work. The magnetic moment $\mu_{eff} = 2.38$ B.M. obtained for α-cobalt phthalocyanine at room temperature is 15% lower than that in β-cobalt phthalocyanine. The ordering and separation between the energy levels of Co^{+2} are discussed on the basis of the experimental data.

I. Introduction

Phthalocyanine compounds are known to exist in at least three polymorphic forms. The β-form is the most stable polymorph, and its molecular orientation and

crystal structure were extensively studied by Robertson[2a] and others.[2b] The other two polymorphs are the α- and γ-forms. Detailed X-ray analyses of the latter two forms have not been performed, because it has not been possible to grow single crystals of these polymorphs. Differentiation between the three polymorphic complexes is best achieved by comparing their characteristic infrared spectra.[3] Most of the accumulated data in the present literature describing the electrical and magnetic properties of the phthalocyanine compounds correspond to the β-form since most of the samples discussed were prepared by sublimation. The β-phthalocyanine (abbreviated β-Pc) is invariably the only polymorph prepared by sublimation methods, which are found to be the most effective purification and crystal growth processes for these metallo-organic complexes.

(1) (a) Taken in part from a dissertation to be presented by J. M. Assour in partial fulfillment of the requirement for a Ph.D degree; (b) RCA Laboratories, Princeton, N. J.

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