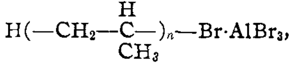
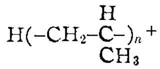
Mechanism of the Polymerization of Propylene with Aluminum Bromide-Hydrogen Bromide Catalyst[1]

BY FRANK R. MAYO AND CHEVES WALLING

The recent excellent experimental work of Fontana and Kidder[2] on the kinetics of the polymerization of propylene by aluminum bromide-hydrogen bromide at about −80° showed that, after the steady rate is obtained, the rate of polymerization is consistent with the equation

$$\frac{-\mathrm{d}[\mathrm{m}]}{\mathrm{d}t} = \frac{kKc[\mathrm{m}]}{1 + K[\mathrm{m}]}$$

where [m] is the monomer concentration, c is the total concentration of catalyst in all forms, K is the equilibrium constant for the reversible formation of a postulated complex formed from a catalyst–monomer complex plus additional monomer, and k is the rate constant for chain lengthening, considered to be rearrangement of the catalyst–polymer–monomer complex into a stable form.

The object of this communication is to present an alternative interpretation of their data. Our scheme assumes (1) that essentially all of the catalyst (or promoter) is bound to the polymer as an un-ionized complex such as  $\mathrm{H(—CH_2—\overset{H}{\underset{CH_3}{C}}—)_{\mathit{n}}—Br{\cdot}AlBr_3}$, (2) that the first rate determining step in the propagation reaction is the dissociation of this complex into  $\mathrm{H(\text{-}CH_2\text{-}\overset{H}{\underset{CH_3}{C}}\text{-})_{\mathit{n}}^{+}}$ and $\mathrm{AlBr_4^-}$, (3) that actual chain propagation involves addition of the carbonium ion and anion to the propylene before recombination of the original ions occurs. Since, in a solvent of low dielectric constant, the dissociated complex will exist as an *ion pair* surrounded by a cage of solvent and propylene molecules, recombination will be kinetically first order, and the situation parallels that suggested by Matheson[3] for peroxide-initiated polymerizations. Thus, the fraction of the dissociations in which the carbonium ion will add a propylene unit before recombining with the negative ion will be $K'[\mathrm{m}]/(1 + K'[\mathrm{m}])$ where K' is the ratio of the rate constant for the reaction of the ion pair with propylene divided by the rate constant for recombination of the ion pair. The over-all rate of polymerization is then

$$\frac{-\mathrm{d}[\mathrm{m}]}{\mathrm{d}t} = \frac{k'K'c\ [\mathrm{m}]}{1 + k'\ [\mathrm{m}]}$$

where k' is the rate of dissociation of the catalyst-polymer complex, c.

The form of the equation shows that an appreciable fraction of the dissociations are accompanied by growth, and also that only one growth step occurs at a time. These requirements are easily met if both ions simultaneously add to the propylene. Experiments with scale models indicate the probability of this course; they also show that the two mechanisms here considered differ only in details. When this interpretation is applied to isobutylene[4], styrene[5] and vinyl ethers[6] the integral orders of these polymerizations with respect to monomer suggest that the fraction of ionizations resulting in chain growth is lower, a result to be expected if the respective complexes ionize more readily but give less reactive carbonium ions.

Our proposed interpretation provides a mechanism for carbonium ion polymerizations in solvents of low dielectric constant similar to that proposed for the polymerization of alkenes by sulfuric acid, the solvolyses of alkyl halides, and the Friedel–Crafts reaction. Further, it accounts more readily than the mechanism of Fontana and Kidder for observations[5,6] that the rates of carbonium ion polymerizations increase very rapidly with the dielectric constant of the solvent. However, our interpretation is inconsistent with one conclusion of Fontana and Kidder, that ΔH for reversible addition of monomer to complex is 8.9 kcal./mole and that K decreases with increasing temperature. In our scheme, this corresponds to the anomaly that the activation energy for simple recombination of two ions is 8.9 kcal./mole *larger* than for addition of propylene to a carbonium ion. Since, in the experiments cited, an appreciable but unknown proportion of catalyst precipitated in an inactive form from each reaction mixture, we suggest that experiments at different temperatures have not yielded correct temperature coefficients, a point which is a critical test of our proposal.

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[1] Contribution No. 95 from the General Laboratories of the United States Rubber Company.

[2] Fontana and Kidder, THIS JOURNAL, **70**, 3745 (1948).

[3] Matheson, *J. Chem. Phys.*, **13**, 584 (1945).

[4] Evans and Meadows, *J. Polymer Sci.*, **4**, 359 (1949).

[5] Pepper, *Trans. Faraday Soc.* **45**, 397, 404 (1949).

[6] Eley and Richards, *ibid.*, 425.

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Investigation of Possible Interactions between Thallium(I) and Thallium(III) in Solution and in the Crystalline Thallium Sesqui-halides

BY HARDEN MCCONNELL AND NORMAN DAVIDSON

The discovery[1] that the rate of radioactive exchange between Tl(I) and Tl(III) in aqueous solutions is slow has prompted us to: (1) examine, by a radiochemical method, whether or not the substances $\mathrm{Tl_2Cl_3}$ and $\mathrm{Tl_2Br_3}$ contain non-equivalent Tl(I) and Tl(III) ions; (2) look for non-additive light absorption[2] in some aqueous solutions containing Tl(I) and Tl(III). Problems (1) and (2) are related because the $\mathrm{Tl_2X_3}$ compounds are more colored than the corresponding TlX or $\mathrm{TlX_3}$ compounds.[3]

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[1] Harbottle and Dodson, THIS JOURNAL, **70**, 880 (1948); Prestwood and Wahl, *ibid.*, **71**, 3137 (1949); see also pp. 226, 205 of "Isotopic Exchange Reactions and Chemical Kinetics," Brookhaven National Laboratory, Patchogue, New York, Dec., 1948.

[2] Whitney and Davidson, THIS JOURNAL, **69**, 2076 (1947).

[3] Benrath, *Z. anorg. Chem.*, **93**, 161 (1915); **136**, 358 (1924).

(1) For the exchange experiment with Tl_2Cl_3, 4 ml. of dilute HCl solution containing 5.2 mg. of dissolved Tl_2Cl_3 and 1.46 mg. of active $TlCl_3$ (containing Tl^{204}) were evaporated nearly but not quite to dryness by evacuation at room temperature for forty-five minutes. It follows from the data of Benrath that under these conditions essentially all of the Tl(I) was initially precipitated as Tl_2Cl_3, and there might be small amounts of $TlCl_2$ or hydrated $TlCl_3$ formed subsequently, depending on the completeness of evaporation.[3] (Furthermore by visual inspection of the precipitate one saw only the characteristic hexagonal yellow flakes of Tl_2Cl_3.)[4] This entire residue, the yellow solid Tl_2Cl_3 and the adhering excess of $TlCl_2$ or $TlCl_3$ (solid or solution), was redissolved in water and divided into two 2-ml. samples. Thallous chromate was precipitated from one portion, using the conditions developed by Harbottle and Dodson,[1] washed, and slurried onto a counting plate. The second sample was reduced with sulfur dioxide so that all the thallium could be precipitated as the chromate and the total activity counted. There was no appreciable self absorption in the samples.

A blank experiment was performed which was identical to the above except that the evaporation to give solid Tl_2Cl_3 was omitted, and the sample was allowed to stand for twenty minutes.

For the Tl_2Br_3 experiment, 30 ml. of a solution containing 1.2 g. of $TlBr_3$ was saturated with inactive TlBr at room temperature to insure the absence of bromine. The solution was then saturated with active TlBr at 50°. Two 10-ml. aliquots of this solution were allowed to cool to room temperature, and the red Tl_2Br_3 precipitated out.[5] The thallous activity was determined with one sample and the total activity with the other. For control measurements, the thallous and total activities of 1-ml. aliquots of the solution at 50° were determined.

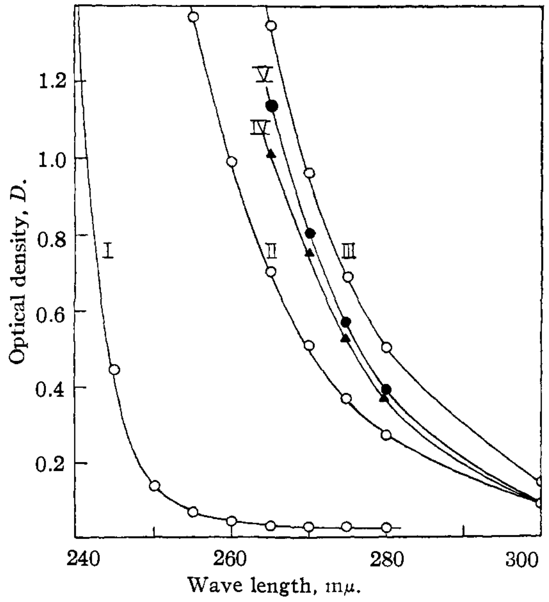

Fig. 1.—The absorption spectra of some thallium(I) and (III) solutions in perchloric acid: I, Tl(I) 0.068 *F;* II, Tl(I) 0.034 *F*, Tl(III) 0.079 *F;* III, Tl(III) 0.157 *F*, I, II, III in 3.2 *F* $HClO_4$; IV, Tl(III) 0.079 *F;* V, Tl(I) 0.113 *F*, Tl(III) 0.079 *F;* IV, V in 1.6 *F* $HClO_4$.

TABLE I

EXCHANGE EXPERIMENTS WITH THALLIUM SESQUI-HALIDES

Experiment	Composition of exchange mixture, mg. Tl(I)	Composition of exchange mixture, mg. Tl(III)	Specific activities,[a] c./min. mg. Tl(I)	Specific activities,[a] c./min. mg. Tl(III)	Ratio of specific activities of Tl(III) and Tl(I)
Solid Tl_2Cl_3	3.12	2.00[b]	31.5	321	10 (±1)
Tl_2Cl_3 control	3.12	2.00[b]	18.6	241	13 (±1)
Solid Tl_2Br_3	32.4[c]	10.8[c]	102	27.8	0.27 ± (0.05)
Tl_2Br_3 control	6.1	18.4	87.7	20.2	0.23 ± (.05)

[a] For the Tl_2Cl_3 experiment, the specific activities were calculated on the basis of the amounts of Tl(I) and Tl(III) added; for the Tl_2Br_3 experiment, see footnote (c). [b] Including 0.96 mg. of active Tl(III). [c] These numbers, estimated from the solubility data of Benrath, are included to indicate the probable size of the Tl_2Br_3 precipitate; only the ratio of activities is important for the interpretation of the experiment.

The experimental results (Table I) are that within the uncertainties of the experiments there is no exchange in the solid state. These uncertainties are due to experimental errors and due to the possibilities of differences between the control experiments and the experiments in which solid Tl_2X_3 compounds were separated as to: (a) degree of homogeneous exchange in solution, (b) degree of induced exchange on precipitation of thallous chromate. For the Tl_2Cl_3 experiment, the calculated ratio of specific activities of Tl(III) and Tl(I) for complete equivalence in the solid is 2.1 accepting the validity of the control experiment (and assuming no exchange between the solid Tl_2Cl_3 and the excess adhering Tl(III)). For the Tl_2Br_3 experiment this ratio is 1.0. Because of the evidence that Tl_2Cl_3 has 64 thallium atoms per unit cell,[6] it is worthwhile to emphasize that our data are not sufficiently accurate to exclude the possibility that a small fraction of the Tl(I) and Tl(III) atoms occupy equivalent positions in the Tl_2X_3 lattice.

(2) Figure 1 exhibits the absorption spectra of some thallium (I) perchlorate, thallium (III) perchlorate, and mixed solutions in 3.2 and 1.6 *F* perchloric acid. Thallium (III) is more colored than Tl(I) and there is no appreciable non-additive absorption in the mixed solutions. The extinction coefficients of Tl(III) calculated from these data (Table II) show that Tl(III) is more colored at lower acidities, suggesting an increased hydrolysis of Tl^{+++} to $Tl(OH)^{+}$ or $Tl(OH)_2^{++}$. Harbottle and Dodson[1] and Prestwood and Wahl[1] have previously suggested such a hydrolysis to explain the variation of the rate of exchange between Tl(I) and Tl(III) with acidity.

TABLE II

EXTINCTION COEFFICIENTS OF Tl(III) AS A FUNCTION OF ACIDITY

λ (mμ)	290	280	270	265
ε (Tl(III))(1.6 *F* $HClO_4$)	2.25	4.6	9.5	13.3
ε (Tl(III))(3.2 *F* $HClO_4$)	1.8	3.25	6.1	8.5

Most of the known cases of interaction absorption in solution are in media containing excess

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(4) Another sample of Tl_2Cl_3 was further identified by a thallium analysis; for a description of the crystalline form, *cf.* Meyer, *Z. anorg. Chem.*, **24**, 354 (1900).

(5) The identification of this substance as Tl_2Br_3 is based on its color and crystalline form corresponding to the descriptions given by Benrath[3] and Meyer[4] and on the solubility data determined by Benrath.

(6) Jerslev and Hägg, *Experientia*, **2**, 495 (1946).

chloride ions. The insolubility of thallous chloride in water and dilute solutions of thallic chloride, and the presence of free chlorine in concentrated thallic chloride solutions (3.5 *F*) in which thallous chloride has an appreciable solubility[3] prevented an exact spectrophotometric study of solutions having significant concentrations of thallous and thallic chlorides. We can report however that as successive portions of solid thallous chloride were added to a 3.4 *F* thallic chloride solution containing some (*ca.* 0.03 *F*) free chlorine, the optical density of the resulting solutions decreased (as the chlorine was removed) and became constant at the values: $\lambda = 380$ mμ, $D = 0.065$; $\mu = 360$ mμ, $D = 0.66$, for a solution that contained 0.04 *F* excess Tl(I). Since the optical densities of the solutions never increased as the TlCl was added, there was probably no significant interaction absorption in the solution.

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The Lactal Ring Structures of Some Synthetic Pyrimidine Nucleosides[1]

BY MARJORIE ZEIGER NEWMARK, IRVING GOODMAN AND KARL DITTMER[2]

The ribosyl, arabinosyl, glucosyl and galactosyl nucleosides of uracil and thymine and the corresponding 5-bromo-uracil derivatives were prepared in our laboratories[3,4] and tested for biological activity[5] on two strains of *Escherichia coli*, two strains of *Neurospora crassa*, a strain of *Lactobacillus casei*, and one of *Streptococcus faecalis* R.

A uracil-requiring mutant of *E. coli* was unaffected by any of the synthetic nucleosides although uracil or natural uridine produced good growth. A uracil-less mutant of *N. crassa* which was shown by Loring to grow well on uracil, uridine or uridylic acid was also unaffected by the synthetic products. Results of studies of *L. casei* and *S. faecalis* R showed a similar lack of biological activity. These studies emphasized the need for complete elucidation of the detailed structure of these synthetic nucleosides.

In order to establish the nature of a possible relationship between structure and activity, a number of naturally occurring and synthetic nucleosides were analyzed by the periodate method as adapted by Davoll, Lythgoe and Todd[6] to determine the ring structures of the sugar component of the nucleosides. In this method glycofuranosyl nucleosides of the pentoses require one mole of periodate per mole of nucleoside for oxidation, whereas glycopyranosides of this type require two moles of periodate. Aldohexoses in the pyranoside form require two moles of periodate for oxidation and liberate one mole of formic acid during the course of the reaction; aldohexoses in the furanoside form also require two moles of periodate for oxidation but liberate no formic acid.

Table I summarizes the results of the periodate oxidation of a number of synthetic pyrimidine nucleosides as well as the naturally occurring pyrimidine nucleosides, uridine and cytidine. All of the synthetic nucleosides here reported possess the pyranoside structure. These results would indicate in part that the known biological activity of uridine and cytidine are dependent upon the furanoside structure.

TABLE I

PERIODATE OXIDATION OF SOME PYRIMIDINE NUCLEOSIDES

N-Glycoside	Moles IO_4^- / Mole glycoside	Moles HCOOH / Mole glycoside
Uridine[a]	1.14	..
Cytidine[a]	1.20	..
1-D-Ribosyl uracil	2.02	..[b]
1-D-Arabinosyl uracil	2.07	..[b]
1-D-Xylosyl uracil	1.89	0.86
1-D-Glucosyl uracil	2.01	0.95
1-D-Galactosyl uracil	2.03	..[b]
1-D-Arabinosylthymine	2.03	..[b]
1-L-Arabinosylthymine	1.92	..[b]
1-D-Galactosylthymine	2.04	0.99
1-D-Glucosylcytosine	1.98	0.88

[a] We are indebted to Dr. H. S. Loring of Stanford University for the samples of uridine and cytidine. [b] The theoretical amount of formic acid expected is 1 mole, but due to limited amounts of material the determinations were not made.

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[1] This work was supported in part by a research grant-in-aid from the National Institutes of Health.

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[3] D. Visser, K. Dittmer and I. Goodman, *J. Biol. Chem.*, **171**, 377 (1947).

[4] D. Visser, I. Goodman and K. Dittmer, THIS JOURNAL, **70**, 1926 (1948).

[5] K. Dittmer, I. Goodman, D. Visser and H. P. McNulty, *Proc. Soc. Exp. Biol. Med.*, **69**, 40 (1948).

[6] J. Davoll, B. Lythgoe and A. R. Todd, *J. Chem. Soc.*, 833 (1946).

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A Complex Praseodymium Fluoride Readily Soluble in Dilute Acids[1]

BY THEODORE P. PERROS AND CHARLES R. NAESER

The insolubility of praseodymium trifluoride in dilute mineral acids is well known. In the course of investigations concerning this compound a complex potassium–praseodymium–fluoride compound, possibly new, which was easily soluble in dilute acids was prepared.

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[1] From the thesis for the M.S. degree of T. Perros, The George Washington University.