We assume that the unimolecular decompositions 6 and 8 have an A factor some 10^4 times greater than that for the bimolecular reactions.

By substituting the values of the x's in the appropriate equations, we obtain the data shown in Table V. The first four substances shown in Table V are in relatively great abundance as compared with the last four; we do not have a great deal of confidence either in the measured or calculated activation energies for these last four substances. In the case of the first four substances, the agreement seems reasonable in view of the experimental difficulties and the approximations made in the calculations. It is noteworthy that the theory predicts that the rate of formation of hydrogen is independent of the initial concentrations of ethylene and deuterium.

The authors are happy to have the opportunity of expressing their gratitude to Dr. F. O. Rice who proposed the problem and made many helpful suggestions during the course of the work.

WASHINGTON, D. C.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, STATE UNIVERSITY OF NEW YORK COLLEGE OF FORESTRY]

The Instantaneous Polymerization of Styrene by Trifluoroacetic Acid[1]

BY J. J. THROSSELL, S. P. SOOD, M. SZWARC[2] AND V. STANNETT

RECEIVED OCTOBER 12, 1955

Trifluoroacetic acid is a powerful initiator for carbonium ion polymerization. Styrene introduced to an excess of trifluoroacetic acid polymerizes instantaneously forming a white, friable, polymeric mass, the yield being close to 100%. On the other hand, addition of small quantities of trifluoroacetic acid to styrene yields a low molecular weight addition product (an ester). Two distinct types of termination should be considered in carbonium ion polymerization: one takes place by returning a proton from carbonium ion to the anion (gegenion), while in the other, the carbonium ion recombines with the gegenion and forms a new covalent bond. The first type of termination characterizes polymerizations initiated by complexes like $BF_3 \cdot CH_3 \cdot COOH$, where the gegenion *cannot* form a covalent bond with the carbonium ion. These terminations are only slightly affected by the surroundings. On the other hand, the second type of termination is very susceptible to the changes of surroundings and takes place in polymerizations initiated by HCl or $CF_3 \cdot COOH$, where the gegenions form covalent bonds with the carbonium ions. Finally, it is pointed out that the properties of molecules in solution depend very much on the nature of the solvation shell. Thus, trifluoroacetic acid molecule in trifluoroacetic acid environment is a powerful proton donor, and its anion is highly stabilized, while the same molecule of acid in hydrocarbon surroundings is a poorer proton donor, forming an anion of low stability.

The understanding of the individual steps of an ionic polymerization is less satisfactory than of those involved in a radical polymerization, although the basic features of the former reaction are now well elucidated.[3] During a search for a convenient source of trifluoromethyl radicals, it was discovered that trifluoroacetic acid is a powerful initiator of carbonium ion polymerization. This was confirmed by the fact that styrene and α-methylstyrene are polymerized instantaneously by this catalyst, while acrylonitrile and other monomers of similar polarity are not at all polymerized. The initiation of polymerization by trifluoroacetic acid does not require any cocatalyst, since the acid *is* itself a proton donor. Accordingly, it was found that traces of water do not affect the rate of the reaction.

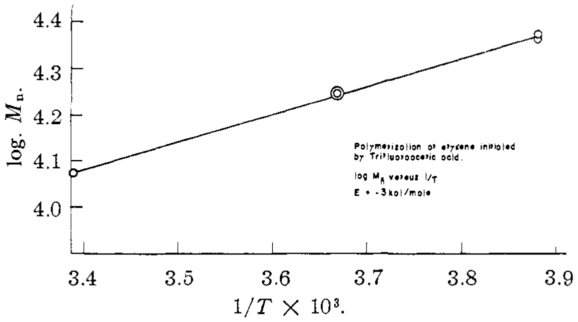

Fig. 1.

The polymerization of styrene by trifluoroacetic acid has been carried out in two ways. In one method, styrene is added dropwise to the stirred excess of pure trifluoroacetic acid; an instantaneous reaction takes place each drop being converted into a white, friable, polymeric mass. The results of some typical experiments are summarized in Table I. The temperature dependence of the molecular weight is found to be exponential and corresponds to a negative "activation energy" of about -3.0 kcal. This relationship is illustrated by Fig. 1.

Alternatively, small amounts of trifluoroacetic acid can be added to an excess of styrene. For reasons which will be made clear later in this paper, the added trifluoroacetic acid is mixed with three volumes of ethylbenzene, and this solution is then stirred into styrene. No high molecular weight polymer is produced under these conditions, although trifluoroacetic acid is consumed rapidly. The rate of the latter reaction increases with increasing temperature, for example, in a mixture of 60 cc. of styrene and 5 cc. of trifluoroacetic acid in 15 cc. of ethylbenzene, only 24% of the acid is consumed in one hour at 0°, but the consumption of acid increases to about 90% in the same period of time at 60°. Vacuum distillation of the reacting material left an oily residue which can be easily hydrolyzed. It was shown that the acid produced in the hydrolysis together with the unconsumed acid account for the total acid added initially. These facts prove that trifluoroacetic acid adds on to sty-

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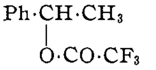
[1] This research was sponsored by Nonr Contract No. 1349-1, and the Dow Chemical Company Fellowship.

[2] To whom requests for reprints should be addressed.

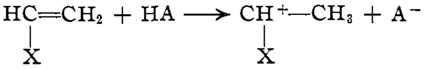
[3] This subject is well reviewed in a recent paper by D. C. Pepper, *Quart. Revs.*, **8**, 88 (1954).

rene, the product being an ester I containing only one or perhaps a few units of styrene.



$$\underset{\textstyle O\cdot CO\cdot CF_3}{Ph\cdot \underset{|}{C}H\cdot CH_3} \quad \text{I}$$

It is desirable to clarify some basic features of carbonium ion polymerization before attempting to interpret the present results. The carbonium ion polymerization is initiated by reaction (1)[4]



$$\underset{\textstyle X}{\underset{|}{HC}}{=}CH_2 + HA \longrightarrow \underset{\textstyle X}{\underset{|}{CH^+}}{-}CH_3 + A^- \qquad (1)$$

which yields the positive carbonium ion, and the negative A^- gegenion. In nearly all the media in which carbonium ion polymerization can be conducted, no separation of ion pairs takes place, since the dielectric constant is too low to decrease sufficiently the electrostatic interaction. The energy change taking place in reaction (1) is represented schematically by Fig. 2, and the endothermicity, ΔH, of this process is given by the sum of three terms

$$\Delta H = \Delta H_g - \Delta H_S - Q \qquad \text{(I)}$$

The first term, ΔH_g, gives the energy change taking place in reaction (1) if the latter is carried out in gaseous phase and yields completely separated ions. Thus

$$\Delta H_g = D(\text{A-H}) - D(\text{H-M}) + I_{\text{HM}} - E_{\text{A}}$$

where D(A–H) is the dissociation energy of the ruptured A–H bond, D(H–M) is the dissociation energy of the H–CH_2CHX bond formed in the process, I_{HM} is the ionization potential of CH_3·CHX radical, and E_{A} the electron affinity of fragment A. The second term $-\Delta H_S$, represents the energy gain in solvation processes, *i.e.*

$$-\Delta H_S = S_{A^-} + S_{HM^+} - S_{HA} - S_M$$

the individual S's representing the solvation energy of the particular species. The last term, Q, represents the coulombic energy of the ion pair, and its magnitude depends on the separation distance of the ions and on the dielectric constant ϵ of the medium

$$Q = (e^2/r)(1 - 1/\epsilon)$$

The last statement needs qualification. The value of the dielectric constant derived from macroscopic experiments need not be identical with the microscopic dielectric constant which should be used partially in determining Q. However, introduction of the concept of the microscopic dielectric constant leads to difficulties in distinguishing between the purely coulombic electrostatic effects due to the charge–charge interaction and those described in terms of solvation processes.

The ionization process is favored by decrease of ΔH. The first term in this equation is determined by the nature of the system proton donor and proton acceptor (*i.e.*, monomer), and is independent of the nature of the surroundings. On the other hand, the last two terms are functions of the surroundings, and hence any discussion of the effects which the medium exerts upon the heat of ionization is reduced to consideration of ΔH_S and Q. The term Q is always positive, and increases with the dielectric constant of the medium.

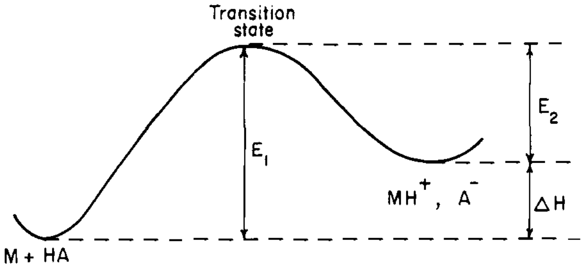
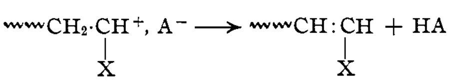


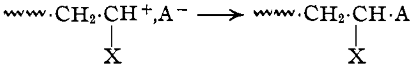
Fig. 2.

Two mechanisms for termination of carbonium ion polymerization need to be considered: the reverse of the initiation process (2)



$$\sim\!\sim CH_2\cdot\underset{\textstyle X}{\underset{|}{CH^+}}, A^- \longrightarrow \sim\!\sim CH{:}\underset{\textstyle X}{\underset{|}{CH}} + HA \qquad (2)$$

and the recombination of the ions (3)



$$\sim\!\sim\cdot CH_2\cdot\underset{\textstyle X}{\underset{|}{CH^+}}, A^- \longrightarrow \sim\!\sim\cdot CH_2\cdot\underset{\textstyle X}{\underset{|}{CH}}\cdot A \qquad (3)$$

The former operates in polymerizations initiated by proton donors yielding anions unable to recombine directly with carbonium ions to form a covalent bond, *e.g.*, in reactions initiated by $BF_3\cdot CH_3COOH$ where the following complex anion is formed: $(BF_3\cdot OCO\cdot CH_3)^-$. Indeed, the work of Evans and Meadows[5a] and of Dainton and Sutherland[5b] proved that this mechanism of termination applies to polymerization of isobutene initiated by $BF_3\cdot H_2O$ or $BF_3\cdot CH_3\cdot COOH$ complex.[6] Experiments[7,8a,8b] which show that no catalyst fragments are present in polymers produced in such systems are additional evidence in favor of reaction (2).

However, if the anion produced can form a covalent bond by recombining with the carbonium ion, termination by equation 3 is operative. The formation of an ester of trifluoroacetic acid in the polymerization of styrene initiated by trifluoroacetic acid points out to this type of termination.[9]

In a polymerization initiated by a catalyst which requires the termination step described by equation 2, the equilibrium constant K_e of the ionization process

$$\text{monomer} + HA \rightleftarrows \text{carbonium ion}^+, A^-$$

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[4] There are unique cases when the carbonium ion polymerization is initiated by transfer of other positive ions than protons. See, for example: D. D. Eley and A. W. Richards, *Trans. Faraday Soc.*, **45**, 425, 436 (1947).

[5] (a) A. G. Evans and G. W. Meadows, *J. Polymer Sci.*, **4**, 359 (1949); (b) F. S. Dainton and G. B. B. M. Sutherland, *ibid.*, **4**, 37 (1949).

[6] Further conclusive evidence is provided by experiments in which D_2O was used instead of H_2O (see Dainton, Tomlison, and Batke, in Carbonium-Ion Polymerization, edited by P. H. Plesch, Heffer, Cambridge, 1953).

[7] Y. Landler, *Rec. trav. chim.*, **68**, 992 (1949).

[8] (a) R. O. Colclough, *J. Polymer Sci.*, **8**, 467 (1952); (b) C. G. Overberger, R. J. Ehrig and D. Tanner, THIS JOURNAL, **76**, 772 (1954).

[9] An analysis of the polystyrene produced in our experiment has been kindly carried out by Dr. B. W. Nippoldt of the Minnesota Mining and Manufacturing Company. Samples corresponding to molecular weight of 17,000 showed 0.40 and 0.29% of fluorine, the calculated value being 0.34%.

is given by the equation

$$K_e = k_i/k_t$$

where k_i denotes the rate constant of initiation, and k_t the rate constant of termination. The increase in the dielectric constant of the solvent increases K_e, and this demands an increase in k_i or a decrease in k_t, or both. The increase of k_i causes an increase in the rate of polymerization (assuming no decrease in the degree of polymerization), and a decrease in k_t should also be reflected in an increase of the degree of polymerization.[10] The work of Pepper[11] demonstrated that an increase in the dielectric constant of the solvent increases the rate of polymerization considerably, but the degree only slightly. Furthermore, the careful work of Overberger and Endres[12] showed that an increase in the dielectric constant of the medium from $\epsilon = 7$ to $\epsilon = 15$ increase the rate of polymerization by a factor of 1000, leaving the molecular weight essentially constant. Making a naive assumption that the change in ϵ changes only the coulombic term Q, we may account well for the observed increase in the rate.[13] These results indicate that the separation of the charge *does* take place in the transition state. Hence, the path leading from the initial state to the transition state involves creation of electric charges, while the path leading from the final state to the transition state involves only small changes in the charge distribution. The increase of dielectric constant increases the rate of initiation, leaving the rate of termination relatively unaffected.

The termination step described by equation 2 is essentially slow, due to considerable chemical inertia resulting from the necessity of rupture of a C–H bond in the carbonium ion. This means that the activation energy of termination is inherent in the nature of the reaction and only somewhat modulated by the environment. Hence, carbonium ion polymerizations terminated by reaction (2) may proceed even in solvents of low dielectric constant and poor solvating abilities.

When the termination proceeds according to equation 3, and if the reaction would take place in the gaseous phase, no chemical inertia would be involved in the termination process, since no activation energy is required for the recombination of ions. However, in solution the necessity for the destruction of the solvation shells introduces an activation energy essential for a slow termination step. Hence, carbonium ion polymerizations terminated by reaction (3) are sensitive to the environment, and yield polymers only in solvents of good solvating power or high dielectric constant.

To illustrate this point, let us quote experiments of Pepper and Somerfield,[14] who studied the polymerization of styrene initiated by HCl. In "poor" solvents they observed only the addition of HCl to the double bond of styrene, while in "good" solvents the polymerization (*i.e.*, the monomer addition to the primary carbonium ion) intervened between the first and the second stage of the hydrohalogenation. The polymerization initiated by trifluoroacetic acid falls into the same category. Trifluoroacetic acid seems to be a "good" solvent, hence, the reaction leads to the formation of polymer when styrene is added to an excess of the acid; styrene is a "poor" solvent and thus only the addition of trifluoroacetic acid to the monomer is observed when trifluoroacetic acid is added to an excess of styrene.

The "good" properties of a solvent may be due to its dielectric characteristic or to its specific solvation abilities. To find which is operative with trifluoroacetic acid, polymerizations of styrene were conducted in mixtures containing trifluoroacetic acid and appropriate solvents. By varying the composition of the mixed solvent, we could adjust the dielectric constant of the medium to any desirable value. The results thus obtained are summarized in Table II, and show conclusively that the increase in the dielectric constant of the medium increases the rate and the degree of polymerization. At the same time, however, it is clear that trifluoroacetic acid is a much more efficient solvent than one would expect judging only by the value of its dielectric constant. We suggest, therefore, that the high activity of trifluoroacetic acid arises from its ability to solvate efficiently the $CF_3 \cdot COO^-$ ions, probably due to the presence of strong hydrogen bonds between $CF_3 \cdot COO^-$ ions and the

TABLE I[a]

Temp., °C.	Conversion, %	Mol. wt.
−15	94.5	23,100
−15	94.6	23,600
0	95.0	17,600
0	97.1	17,600
22	94.6	11,850

[a] The experiments were performed with 10 cc. of trifluoroacetic acid into which 1 cc. of styrene was added dropwise. The molecular weight was determined by measuring the intrinsic viscosity in toluene at 30°, using the relationship[15]

$$M_{\bar{n}} = 167{,}000(\eta)^{1.37}$$

TABLE II[a]

Composition of the mixture[b]	ϵ	Conversion, %	$M_{\bar{n}}$
12 TFA	10	100	17,600
12 TFA .. 18 EB	5	1.5	....
12 TFA + 3 NB + 15 EB	9	21	3,230
12 TFA + 4.2 NB + 13.8 EB	10	31	3,030
12 TFA + 6 NB + 12 EB	13	45	3,190
12 TFA + 18 NB ..	28	100	7,920

[a] The experiments were performed by dripping 3 cc. of styrene into polymerizing mixture at 0°. The reaction is over when the added styrene is dispersed finally in the polymerizing medium, and the low conversion indicates that the remaining monomer was "esterified" by adding trifluoroacetic acid across the double bond. [b] TFA, trifluoroacetic acid; NB, nitrobenzene; EB, ethylbenzene.

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[10] The degree of polymerization is given by the equation

$$\text{d.p.} = k_p(\text{M})/k_t$$

(assuming no complications due to chain transfer reactions). The rate constant k_p is probably only slightly affected by the nature of the surrounding, since the propagation step does not change the electric charges present in the system.

[11] D. C. Pepper, *Nature*, **164**, 655 (1949); *Trans. Faraday Soc.*, **45**, 397, 404 (1945).

[12] C. G. Overberger and G. F. Endres, *J. Polymer Sci.*, **16**, 283 (1955).

[13] Making this assumption, we calculate the increase in the rate as expt. $\{(e^2/r)(1/7 - 1/15)/k_T\}$. This is of the order of 1000 for a reasonable value of $r = 5A$.

[14] D. C. Pepper and A. E. Somerfield, *Chem. and Ind.*, 42 (1954).

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

molecules of trifluoroacetic acid. Thus, the $CF_3 \cdot COO^-$ ion in trifluoroacetic acid is not easily available for the termination step, while the same ion in hydrocarbon surroundings may easily recombine with its gegenion.

In conclusion, we would like to point out that trifluoroacetic molecules behave like different species in different surroundings (the same applies, of course, to many other systems). The molecules of trifluoroacetic acid in trifluoroacetic acid surrounding are probably highly associated and are strong proton donors, because the equilibrium

$$(CF_3 \cdot COOH)_{n-1} \rightleftarrows (CF_3 \cdot COOH)_n \cdot CF_3 \cdot COO^- + H^+$$

is shifted to the right by the stabilizing effect of trifluoroacetic acid on the CF_3COO^- ion. On the other hand, the same molecules in other surroundings are weaker proton donors, because the respective ion is poorly stabilized. For example, addition of trifluoroacetic to styrene produces simultaneously a polymer and a low molecular weight ester. A closer inspection demonstrated that the polymer results from the interaction of styrene with bulk trifluoroacetic acid (*i.e.*, with the mass introduced before it was dispersed completely), while the low molecular weight ester results from the interaction of the dispersed acid with styrene. For this reason, in the experiments described previously, trifluoroacetic acid was added to styrene in the form of its solution in ethylbenzene.

Experiments in which styrene was added to trifluoroacetic acid in form of small and large droplets showed that the size of the droplets did not affect the per cent. of conversion or the molecular weight of the product (see Table III). This means that the time of growth of a polymeric ion is much shorter than the time needed for dispersion of even small droplets.

TABLE III

ADDING STYRENE TO TRIFLUOROACETIC ACID AND VARYING THE SIZE OF DROPLETS ($T = 0°$).

No. of drops per cc.	% conversion	Molecular weight
95	89	16,700
30	87	16,000
14	88	16,000
stream	96	17,600

The inorganic chemist is well aware of the fact that a description of a system as, *e.g.*, "Ferric ion," is inadequate for its characterization, since the solvation shell changes profoundly its chemical property. For example, the exchange reaction between radioactive ferric and non-radioactive ferrous exhibits not only a different rate when different anions are present in the system, but sometimes proceeds by entirely different mechanism. We hope that this paper will demonstrate that the solvation shell is equally important in the realm of organic chemistry, and explain why A + B is not always equal to B + A.

SYRACUSE, NEW YORK

[CONTRIBUTION FROM THE METCALF CHEMICAL LABORATORIES OF BROWN UNIVERSITY]

The Kinetics and Mechanism of the Decomposition of Caro's Acid. I

BY DONALD L. BALL AND JOHN O. EDWARDS

RECEIVED SEPTEMBER 26, 1955

The kinetics and mechanism of the aqueous decomposition of Caro's acid has been investigated. Both titration and kinetic data indicate that the second ionization constant is about 4×10^{-10}. Both spontaneous and catalytic paths for decomposition were observed; however, the latter path can be eliminated by addition of EDTA. The rate of spontaneous decomposition is second order in peroxide concentration and the *p*H dependence indicates the presence of one proton along with two divalent anions in the activated complex. The temperature dependences of the rates at high and low *p*H values allow the calculation of ionization and activation parameters.

Introduction

The chemistry of peroxymonosulfuric acid (Caro's acid) is less well-understood than the chemistries of the two related compounds, peroxydisulfuric acid and hydrogen peroxide. Caro's acid is highly reactive; in aqueous solution around neutrality it decomposes rapidly. It readily oxidizes many inorganic reagents and it attacks most organic compounds. Pure, stable[1] salts of Caro's acid have never been prepared.

Although the structure of Caro's acid has never been elucidated conclusively,[2] it is generally accepted that it consists of a central sulfur atom that is surrounded tetrahedrally by a perhydroxyl group, a hydroxyl group and two oxygen atoms. The acid is dibasic; one proton is highly acidic and the second is weakly acidic.

The present study concerns the kinetics and mechanism of the spontaneous decomposition of Caro's acid to give oxygen and sulfate ion. In addition, the second ionization constant of Caro's acid has been measured by means of both *p*H titration data and kinetic data.

Experimental

Preparation.—Caro's acid was customarily prepared by the reaction of 90% hydrogen peroxide and chlorosulfonic acid at a temperature between −40 and −50°.[3] The liquid product consists of an upper layer (about one-third of the total volume) and a lower layer. It was reported[3] that Caro's acid is a crystalline solid melting at 45°; however, large amounts of sulfate were present as an impurity in our preparations. Investigations[4] revealed that the upper layer contains chlorine, sulfuric acid, small amounts of Caro's acid, and some unreacted chlorosulfonic acid; this layer was discarded. The bottom layer contains Caro's acid, sulfuric acid and hydrogen chloride. The product was purified further by the vacuum removal of the by-product,

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[1] (a) T. S. Price, *J. Chem. Soc.*, **89**, 54 (1906); (b) **91**, 536 (1907); (c) "The Per-acids and Their Salts," Longmans, Green and Co., London, 1912, p. 53.

[2] A. Simon and G. Kratzsch, *Z. anorg. Chem.*, **242**, 369 (1939).

[3] J. D'Ans and W. Friederich, *Ber.*, **43**, 1880 (1910).

[4] A. Alexio, unpublished experiments at Brown University.