The Role of Monomer Solvation and Counterion Complexation in the Cationic Polymerization of Vinyl Monomers

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ABSTRACT

The charge-transfer complexes between π-donors and stable carbenium ion salts as model systems characterizing the intermediate state of the cationic propagation reaction are detected by UV-VIS spectroscopy. The equilibrium constants and thermodynamic data are discussed. By the use of spectroscopic investigations and conductivity measurements, CT complexes between counter ions and organic π-acceptors, Lewis acids, or acceptor solvents have been proved. The results led to interpretation of the propagation reaction as a competing interaction between the chain carriers and the monomer, the counterion, and the solvent.

INTRODUCTION

Scheme 1 visualizes the supposition for the course of cationic polymerizations. According to Scheme 1, an electrophilic reaction center $X^{\oplus}$, which is electrostatic stabilized by a counterion $Y^{\ominus}$, must interact with a π-, n-, or σ-donor, whereas a covalent bond is formed and the electrophilic center $X^{\oplus}$ is renewed under chain

Electrophilicity ▰▰▰▰▰▰➤ Nucleophilicity ▰▰▰▰▰▰➤

$$X^{\oplus} \sim H^{\oplus} > C^{\oplus} > O^{\oplus} > S^{\oplus} > N^{\oplus} \qquad Y^{\ominus} \sim Cl^{\ominus} > Br^{\ominus} > J^{\ominus} \gg AlCl_4^{\ominus} > BF_4^{\ominus} > SbF_6^{\ominus}$$

$$\text{cat.polym.:} \quad X^{\oplus} \quad Y^{\ominus} \longrightarrow \text{initiation ;propagation- reaction}$$

$$R{\overset{}{\underset{}{>}}}C=C{\overset{'}{\underset{'}{<}}} ; \; \overset{\bar{O}}{\square} ; \; \overset{\delta^+}{R} - \overset{\delta^-}{Y} ; \quad \overset{NC}{\underset{NC}{>}}C=C{\overset{CN}{\underset{CN}{<}}} ; \; MtY_n ; \; \overset{\delta^-}{R} - \overset{\delta^+}{X}$$
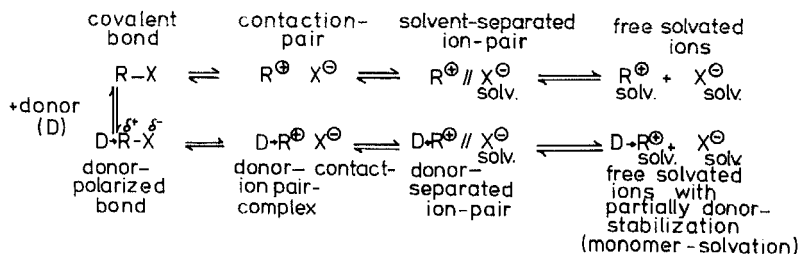$$\qquad\qquad (C-Cl) \qquad\qquad\qquad\qquad\qquad (C-H)$$
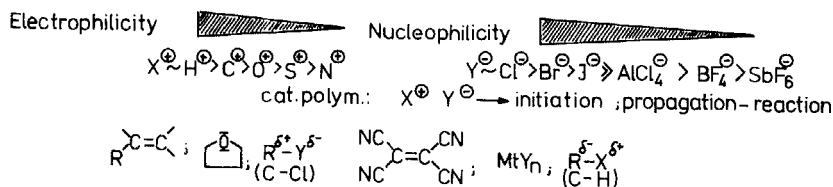
SCHEME 1. Supposition for the course of cationic polymerizations.

prolongation. In principle this reaction step is comparable for both
initiation and for the propagation reaction if $X^{\oplus}$ is a proton (initia-
tion by protonic acids) or a carbeniumion (initiation by stable car-
beniumion salts). Also, the interaction between $X^{\oplus}$ and the σ-donor
R-Y, shown in Scheme 1, which sets free $R^{\oplus}$ and so gives rise to
initiation of the polymerization, may be seen under these aspects.
The interaction between $X^{\oplus}$ and π- and n-donors normally leads to
the vinyl-type polymerization of olefins or diolefins as well as to
heterocyclic ring-opening polymerization. Not only initiation but
also chain propagation raises the probability for a covalent bond
formation with the electrophilicity of $X^{\oplus}$. The precoordinated inter-
action of $X^{\oplus}$ with the monomer has been designated in publications
of Furukawa [1] and Overberger [2] as monomer solvation.

Particularly for the propagation reaction, the probability for bond
formation with another monomer is strongly dependent on the nature
of the counterion. Chain propagation can be expected only in the
presence of counterions with sufficient small nucleophilicity (compare
the sequence in Scheme 1). The counterions may reach additional
stability by complex formation with acceptors, which means with
added organic π-acceptors [3], in the reaction system with Lewis
acids acting as ν-acceptors or suitable solvents acting as σ-acceptors.

In contrast to radical polymerization, in cationic polymerization an
exact characterization of possible interactions with the chain carrier
(the counterion) is rendered more difficult by reason of the ionization-
dissociation behavior [4] of the active species. The degree of charge
separation of the propagating species varies strongly. Scheme 2
contains a system of cooperative equilibria relating to the interaction
of the electrophilic center with a donor (D), whereas the quantification
of Scheme 2 by experimental methods is difficult to realize.

	covalent bond	contaction– pair	solvent-separated ion-pair	free solvated ions
	$R-X$	$R^{\oplus} \; X^{\ominus}$	$R^{\oplus} /\!/ X^{\ominus}_{solv.}$	$R^{\oplus}_{solv.} + X^{\ominus}_{solv.}$
+donor (D)	$\Updownarrow$			
	$D{\to}\overset{\delta^+}{R}-\overset{\delta^-}{X}$	$D{\to}R^{\oplus} \; X^{\ominus}$	$D{\to}R^{\oplus} /\!/ X^{\ominus}_{solv.}$	$D{\to}R^{\oplus}_{solv.} \; X^{\ominus}_{solv.}$
	donor– polarized bond	donor– contact- ion pair- complex	donor– separated ion-pair	free solvated ions with partially donor– stabilization (monomer–solvation)

SCHEME 2. System of cooperative equilibria for the ionization-
dissociation scheme in the case of interaction with additional donor.

TABLE 1. Characteristic Data for Solid EDA-Complexes between $Ph_3C^{\oplus} SbCl_6^{\ominus}$ and π-Donors

Donor	Color	λ_{max} (nm) (reflection spectra)	T_{decomp} (°C)	ΔH (kJ/mol donor)
Benzene	Light orange	555.6	80	35.36
Toluene	Yellow-orange	531.9	57	27.15
Styrene	Orange	558.0	59	-
p-Xylene	Orange	549.5	48	14.33
Mesitylene	Red	560.5	98	31.47
Naphthalene	Dark violet	621.9	-	-

In real systems the situation becomes overcomplicated since as donors may function as monomers as well as solvent molecules and the propagation reaction is seen to be a competition between the monomer, the solvent, and the counterion in their interaction with the electrophilic center.

For a better qualitative understanding of monomer solvation and counterion complexation, we have investigated the different equilibria of interactions where the stable carbeniumion salts have been used as models for chain carriers and counterions.

MONOMER-SOLVATION AT THE ELECTROPHILIC REACTION CENTER

Solutions of $Ph_3C^{\oplus} SbCl_6^{\ominus}$ in dichloroethane or in methylene chloride show a long-wave CT absorption after the addition of π-donors [5]. Increasing concentration of the donor and decreasing polarity of the solvent by the addition of CCl_4 in some cases leads to the formation of solid complexes [6]. Table 1 contains the λ_{max} values from reflection spectra as well as data on the thermal degradation of the solid complexes.

Exhaustive investigations of the complex stoichiometry in solution [7] hint at a 1:1 ratio between the acceptor and the π-donor, as shown in Fig. 1 for the complex formation between $Ph_3C^{\oplus} FeCl_4^{\ominus}$ and p-xylene determined by the Job method [8].

If one raises the acceptor strength of the electrophilic center by substitution of the phenyl groups, with respect to the same donor a bathochrome shift of the CT absorption was observed, whereas in Fig. 2 a linear relation between $\tilde{\gamma}_{CT}$ and the sum of the substitutent constants by Hammett ($\Sigma\sigma_p$) has been found.
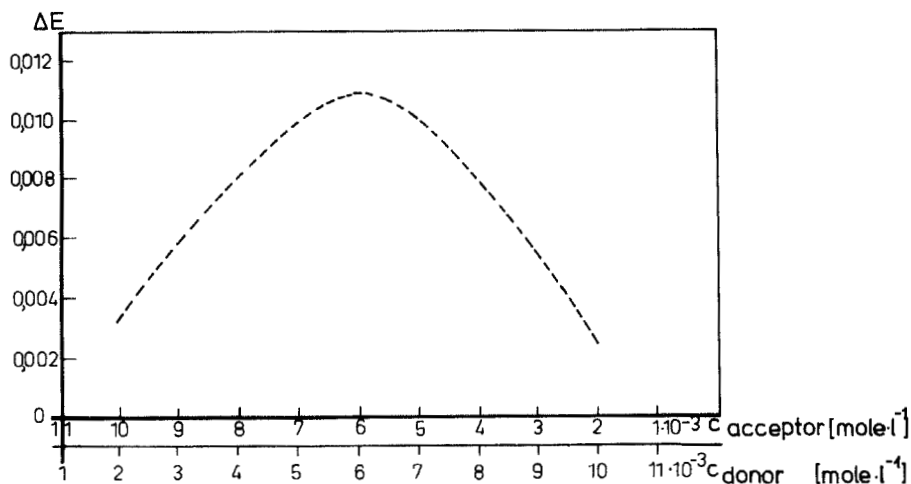
FIG. 1. Determination of the complex composition determined by the JOB-method [8] for $Ph_3C^{\oplus} FeCl_4^{\ominus}$/p-xylene. T = 293 K; λ = 533.3 nm; solvent: CH_2Cl_2.
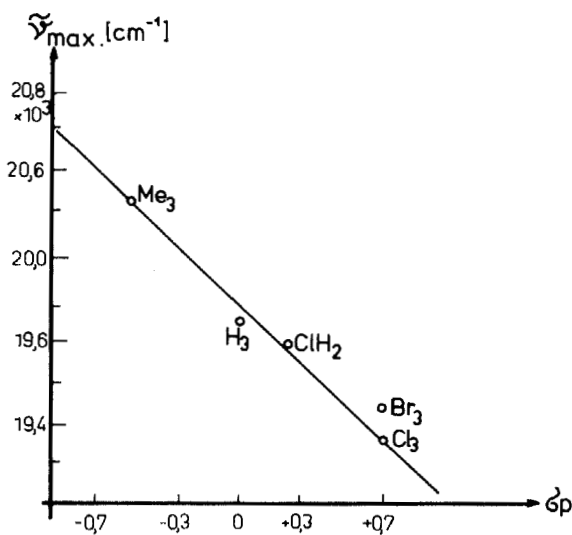

FIG. 2. Relationship between the acceptor character of the cation ($\tilde{\nu}_{CT}$) and $\Sigma\sigma_p$ of the substituents in the p-position for $(p\text{-}X\text{-}Ph)_3\text{-}C^{\oplus} FeCl_4^{\ominus}$/mesitylene.

TABLE 2. Spectroscopic Data for the EDA Complex Formation between Substituted $Ph_3C^{\oplus}$ Salts and Mesitylene. Solvent: CH_2Cl_2

Acceptor	$FeCl_4^{\ominus}$			$SbCl_6^{\ominus}$		
	λ_{max} (nm)	$\tilde{\nu}_{max}$ (cm^{-1})	E_{CT} (kJ/mol)	λ_{max} (nm)	$\tilde{\nu}_{max}$ (cm^{-1})	E_{CT} (kJ/mol)
$(p\text{-}Br\text{-}Ph)_3C^{\oplus}$	519	19,280	230.87	(492)	(20,320)	243.02
$(p\text{-}Cl\text{-}Ph)_3C^{\oplus}$	523	19,120	228.77	512	19,520	233.80
$(p\text{-}Cl\text{-}Ph)Ph_2C^{\oplus}$	511	19,560	234.22	508	19,680	235.48
$Ph_3C^{\oplus}$	509	19,640	235.06	507	19,720	235.90
$(p\text{-}CH_3\text{-}Ph)_3C^{\oplus}$	(492)	(20,320)	246.37	(487)	(20,520)	245.53

As seen from Table 2, the change of relative stable counterions ($FeCl_4^{\ominus}$, $SbCl_6^{\ominus}$) has no drastic effect on the position of the CT bond, considering that the absorption bands are very broad and that the exactness of the measurements is limited. Therefore we conclude there are solvent-separated ion-pairs and free solvated ions in methylene chloride.

On the other hand, it follows from analogous investigations of tropyliumion salts and π-donors in dichloroethane that the stronger differences of CT absorption depend on the counterion (see Table 3). The lower dissociation ability of these salts in consequence of the stronger interaction of the "harder" cation, particularly with small and therefore also "harder" counterions, seems to compete with the interaction between cation and π-donor [9]. As comparison with the $Br^{\ominus}$ in Table 3 shows, the nucleophilicity of the anion has to be taken into consideration in addition to the anion radius [10].

At the same acceptor strength and with varied π-donicity, expressed by the potential of ionization of the donor, one finds the expected bathochrome shift with decreasing I_{pot}. This is shown in Fig. 3 for methyl-substituted aromatic compounds and $Ph_3C^{\oplus}$ $FeCl_4^{\ominus}$ as acceptor in methylene chloride as solvent.

Tables 4 and 5 contain the spectroscopically determined equilibrium constants K_c as well as thermodynamic data for the complex formation between the acceptors $Ph_3C^{\oplus}SbCl_6^{\ominus}$, $Ph_3C^{\oplus}FeCl_4^{\ominus}$, and methyl-substituted aromatic compounds (Table 4) and p-substituted styrenes (Table 5) acting as π-donors.

The K_c values increase in general with increasing strength of the donor. The enthalpy and entropy values hint at competition between electronic and steric effects in the approach of the π-donors to the

TABLE 3. CT Maxima of π-Donor Tropyliumion Complexes Depending on the Anion Variation. T = 298 K; solvent: $(CH_2)_2Cl_2$

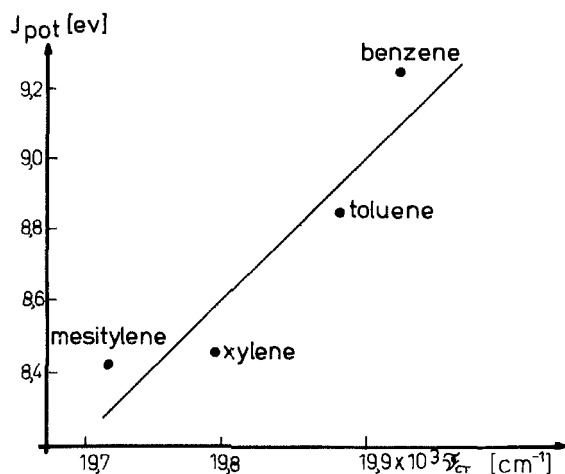| Anion	$1/r$	Acenaphthene	Anthra-cene	Hexamethyl-benzene	Naphtha-lene
		$\nu_{CT} \times 10^{-3}/cm^{-1}$			
$BF_4^{\ominus}$	0.714	20.0	18.4	22.8	23.2
$AsF_6^{\ominus}$	0.541	19.9	18.2	22.3	22.9
$SbCl_6^{\ominus}$	0.412	19.8	18.08	22.4	22.8
$Br^{\ominus}$	0.513	–	18.71	23.15	23.15

FIG. 3. Relationship between the ionization potential (I_{pot}) of the donors (methyl substituted benzenes) with the constant acceptor $Ph_3C^{\oplus} FeCl_4^{\ominus}$.

TABLE 4. Thermodynamic Data for the EDA Complex Formation between Methyl-Substituted Benzenes and Trityl Salts in CH_2Cl_2. The K_c Values Are Calculated for 273 K

Donor	$Ph_3C^{\oplus}SbCl_6^{\ominus}$			$Ph_3C^{\oplus}FeCl_4^{\ominus}$		
	K_c (L/ mol)	ΔH (kJ/ mol)	ΔS (J/ mol K)	K_c (L/ mol)	ΔH (kJ/ mol)	ΔS (J/ mol K)
Benzene	0.35	-5.03	-37.71	0.27	-4.61	-28.07
Toluene	0.88	-15.50	-58.66	0.70	-5.03	-21.79
p-Xylene	1.88	-23.46	-80.87	2.55	-9.22	-26.40
Mesitylene	2.50	-11.31	-33.94	3.26	-5.45	-10.48
Durene	5.00	-6.70	-10.48	-	-	-
Hexamethyl-benzene	35.00	-10.01	-7.54	67.57	-13.41	-14.67

TABLE 5. Spectroscopic and Thermodynamic Data for the Complex Formation between $Ph_3C^{\oplus}FeCl_4^{\ominus}$ and p-Substituted Styrenes $p-X-C_6H_4-CH=CH_2$. T = 273 K; solvent: CH_2Cl_2

Donor X	$\tilde{\nu}_{max}$ (cm^{-1})	K_c (L/mol)	ΔG (kJ/ mol)	ΔH (kJ/ mol)	ΔS (J/ mol K)	$\sigma_{p(x)}$
I	(19,840)	2.7	-2.1	-15.5	-49.02	0.18
Br	(19,800)	4.0	-3.14	-16.34	-48.60	0.23
Cl	(19,760)	4.7	-3.35	-13.41	-36.03	0.23
F	(19,760)	2.3	-2.1	-8.38	-23.46	0.06
H	19,340	5.0	-3.77	-5.87	-7.96	0

electrophilic center. Further, one can see from Tables 4 and 5 that the entropy values are less negative as is to be expected, if one donor molecule "sets free" more than one solvent molecule. Expressed in other words, it seems that in the course of the complex formation, one order is replaced by another one. Transfer to the viewpoint of cationic polymerization gives rise to the conclusion that in a solvent-separated ion pair, solvation by the solvent may be replaced partially by "monomer solvation" as a precoordinating orientation of the reactants before the propagation reaction.

TABLE 6. CT Maxima of $C_7H_7^{\oplus}BF_4^{\ominus}$ with π-Donors in Solvents of Different Donor Number (DN; Ref. 16)

Donor	$\tilde{\nu}_{CT} \times 10^{-3}/cm^{-1}$		
	1,2-Dichloroethane	Nitromethane	Acetonitrile
Toluene	-	-	32.34
p-Xylene	-	-	31.05
Mesitylene	27.36	-	28.63
Phenyl methyl ether	25.2	25.84	27.02
Naphthalene	23.2	24.88	25.08
Hexamethyl benzene	22.8	23.84	24.04
1,4-Dimethyl-benzene	20.92	22.64	22.84
Acenaphthene	20.0	21.4	21.7
Anthracene	18.4	19.8	20.44
Donor number	0	2.7	14.1

The role of the solvent as a "competing donor" (to the monomer and the counterion) obviously is shown in Table 6 [9]. With the same donor in dichloroethane (donor number 0), CT absorption has been found in general to be long-wave, whereas with increasing donor number the CT absorption is shifted to be more hypsochrome. With this evidence of specific cation solvation by solvents of a partial donor nature, the permissibility of conclusions on the mechanism of the cationic polymerization derived from investigations of solvent mixtures seems to be doubtful [10].

Finally, repeated evidence of negative coefficients of temperature of the propagation rate should be mentioned. This fact hints at the role of preferred monomer solvation at lower temperatures and increasing contraction of the ion pairs by "desolvation" of the monomer or of solvent molecules.

COUNTERION COMPLEXATION BY ACCEPTORS OF A DIFFERENT NATURE

In the Introduction the essential influence of the counterion on the course of polymerization was mentioned. Many publications consider

TABLE 7. Examples for the Donor–Acceptor Stabilization of Counterions in the Mechanism of Cationic Polymerizations [10][a]

Donor	Acceptor	Stabilized anion	Example
$X^{\ominus}$	MtX_n	$MtX_{n+1}^{\ominus}$	$HO^{\ominus} + MtX_n \rightleftharpoons MtX_n OH^{\ominus}$
$X^{\ominus}$	X_2	$X_3^{\ominus}$	$J^{\ominus} + J_2 \rightleftharpoons J_3^{\ominus}$, i.e., $J_{n+1}^{\oplus}$
$X^{\ominus}$	HX	$HX_2^{\ominus}$	$Ph_3CCl + HCl \rightleftharpoons Ph_3C^{\oplus}\cdots HCl_2^{\ominus}$
$X^{\ominus}$	$HOPh$	$X^{\ominus}\cdots HOPh$	$Ph_3CCl + HOPh \rightleftharpoons Ph_3C^{\oplus}\cdots Cl^{\ominus}\cdots HOPh$
$X^{\ominus}$	EA	$X^{\ominus}\cdots EA$	$Br^{\ominus} + TCNE \rightarrow Br^{\ominus}\cdots TCNE$
$MtX_{n+1}^{\ominus}$	EA	$MtX_{n+1}^{\ominus}\cdots EA$	$SbF_6^{\ominus} + TCNE \rightleftharpoons SbF_6^{\ominus}\cdots TCNE$
$MtX_{n+1}^{\ominus}$	MtX_n	$Mt_2X_{2n+1}^{\ominus}$	$SbF_6^{\ominus} + SbF_5 \rightleftharpoons Sb_2F_{11}^{\ominus}$
$MtX_{n+1}^{\ominus}$	$HOPh$	$MtX_{n+1}^{\ominus}\cdots HOPh$	$BF_4^{\ominus} + HOPh \rightleftharpoons BF_4^{\ominus}\cdots HOPh$
$MtX_n^{\ominus}$	MtX_n	$MtX_{n+1}^{\ominus}$	$2AlBr_3 \rightleftharpoons Br_2Al^{\oplus} + AlBr_4^{\ominus}$

^{a}EA = electron acceptor. TCNE = tetracyanoethylene.

TABLE 8. Conductometrically and Spectroscopically Determined Overall Decay Rate Constants of $Ph_3C^\oplus MtX_nY_m^\ominus$ Salts. Solvent: 1,2-dichloroethane; T = 298 K; $C_{salt} = 10^{-4} \ldots 10^{-5}$ mol/L

$MtX_nY_m^\ominus$	k_z (conduct.) (s^{-1})	k_z (spectros.) (s^{-1})
$PF_6^\ominus$ [a]	3.5×10^{-3}	1.9×10^{-3} [b]
$AsF_6^\ominus$	$\sim 1 \times 10^{-8}$	$\sim 1 \times 10^{-8}$
$SbF_6^\ominus$	$< 1 \times 10^{-10}$	$< 1 \times 10^{-10}$
$SbCl_6^\ominus$	2.15×10^{-5}	2×10^{-5}
$SbCl_5Br^\ominus$	2.25×10^{-5}	4×10^{-4}
$SbCl_3Br_3^\ominus$	2.4×10^{-3}	3.1×10^{-3}
$SbClBr_5^\ominus$	4.3×10^{-3}	2.8×10^{-2}
$SbBr_6^\ominus$	4.4×10^{-2}	8×10^{-2}
$SnCl_5^\ominus$	3.47×10^{-5}	3.5×10^{-6}
$SnCl_4Br^\ominus$	4.1×10^{-5}	6.2×10^{-6}
$SnClBr_4^\ominus$	0.9×10^{-4}	5.2×10^{-5}
$SnBr_5^\ominus$	1.87×10^{-4}	6.1×10^{-5}
$BF_4^\ominus$ [a]	1.2×10^{-6}	$\sim 1 \times 10^{-6}$
$AlCl_4^\ominus$ [a]	4.4×10^{-3}	6.1×10^{-4} [b]
$AlBr_4^\ominus$ [a]	6.7×10^{-3}	1.1×10^{-3} [b]
$InCl_4^\ominus$	$< 1 \times 10^{-8}$	$< 1 \times 10^{-8}$
$TiCl_5^\ominus$ [a]	1.08×10^{-3}	1.8×10^{-4} [b]
$FeCl_4^\ominus$	$< 1 \times 10^{-8}$	$\sim 1 \times 10^{-8}$
$FeCl_3Br^\ominus$	1.5×10^{-6}	$\sim 1 \times 10^{-6}$

[a] Extremely sensitive to water.
[b] Measured under high vacuo conditions.

the necessary stability of the counterions but without quantitative information on the real meaning of it. Several counterions are found to be particularly stable ($SbF_6^\ominus$, $BF_4^\ominus$, etc.); others find additional stabilization by interaction with different electron acceptors (EA). Table 7 contains examples of possible counterion stabilization by acceptors.

Quantification of the nature of counterions by additional stabilization require better knowledge of the kinetic stability of the counterions.
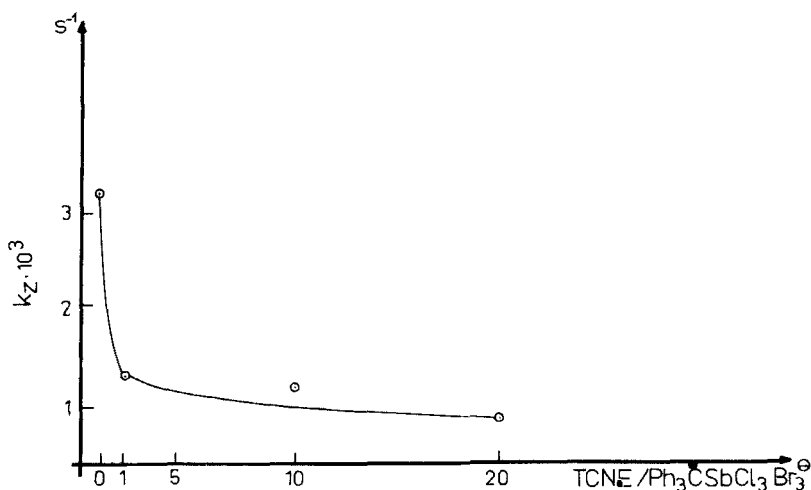
FIG. 4. Dependence of the spectroscopically determined overall decay rate constant k_z of $Ph_3C^{\oplus}SbCl_3Br_3^{\ominus}$ from the added TCNE share. T = 298 K; solvent: $(CH_2)_2Cl_2$.

Again, with carbeniumion salts as the model system for cationic polymerization, the overall decay rate constant k_z has been determined by spectroscopic and conductometric methods for the reaction [12]

$$Ph_3C^{\oplus} + MtX_{n+1}^{\ominus} \xrightarrow{k_z} Ph_3C-X + MtX_n$$
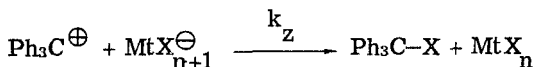
The results are collected in Table 8. The agreement of k_z values taken by both methods shows their ability to measure the kinetic stability of the counterions.

Figure 4 shows that k_z of the $SbCl_3Br_3^{\ominus}$ ion depends on the tetracyanoethylene concentration of the solution [10].

Notice that a relatively small amount of the acceptor causes a remarkable stabilization of the counterion, which hints at the formation of "acceptor-separated" ion pairs [3].

This EDA complex formation is to be taken into account in the case of Lewis acid initiation if the strong ν-acceptor is in excess. In Fig. 5 are shown the results of conductometric measurements of the influence of Lewis acids on the dissociation of $Ph_3C^{\oplus}BF_4^{\ominus}$.

From Fig. 5 it can be learned that the most evident change of conductivity takes place at an approximate mole ratio of 1:1, and from
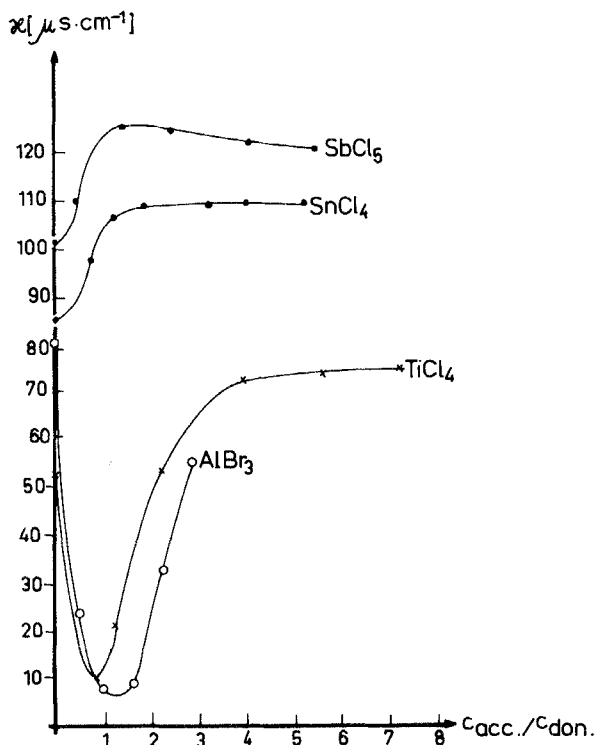
FIG. 5. Dependence of specific conductivity χ of $Ph_3C^{\oplus}BF_4^{\ominus}$ from the addition of Lewis acids. T = 298 K; solvent: $(CH_2)_2Cl_2$; $C_{acc.}$ = C_{MtX_n}; $C_{Ph_3C^{\oplus}BF_4^{\ominus}}$ = 2.2×10^{-3} to 3.4×10^{-3} mol/L.

this it is concluded that there is a 1:1-complex formation between the counterion $BF_4^{\ominus}$ and the Lewis acids [13].

Additional stabilization of counterions may be realized by using suitable solvents with a predominantly acceptor nature. In Table 9 is shown the change of CT absorption of $(i\text{-}amyl)_4$ $N^{\oplus}I^{\ominus}$ → TNB (tri-nitrobenzene) complexes by solvent variation [14]. Table 9 also contains the linear correlation between ν_{CT} and the acceptor number (AN) given by Gutmann [15, 16]. The scale of exactness with B = 0.92 is quite satisfactory. Of course, no correlation has been found with the donor number (DN). One can learn from Table 9 that for acceptor solvents, i.e., $CHCl_3$, CH_2Cl_2, or isopropanol, there is a strong hypsochrome shift of the CT band, which obviously is to be explained by a decrease of the HOMO of the $I^{\ominus}$ anion by specific solvation and an increase of the ionization potential [17]. Evidence for this

TABLE 9. CT Maxima (ν_{CT}/cm^{-1}) of $I^{\ominus} \longrightarrow$ TNB Complexes in Different Solvents. T = 298 K; cation: $(i\text{-amyl})_4N^{\oplus}$; correlation equation: $\nu_{CT(I^{\ominus} \longrightarrow TNB)} \times 10^{-3}\ cm^{-1} = 19.6 + 0.16\ AN$; B = 0.92; n = 8

Solvent	$\nu CT(I^{\ominus} \longrightarrow TNB)$ $\times 10^{-3}/cm^{-1}$	AN	DN
CCl$_4$	21.4	8.6	-
CHCl$_3$	23.0	23.1	-
THF	21.1	8.0	20.0
CH$_2$Cl$_2$	22.6	20.4	-
(CH$_3$)$_2$CHOH	25.0	33.5	-
(CH$_3$)$_2$CO	21.2	12.5	17.0
CH$_3$CN	23.1	18.9	14.1
DMSO	22.4	19.3	29.8

competition of two acceptors (TNB as solvent) has been experimentally verificated in the case of strong nucleophilic counterions, whereas metalhalogeno anions in general shows a stronger "internal" stabilization [18, 19].

CONCLUSIONS ON THE MECHANISM OF THE PROPAGATION REACTION

On the basis of the model system used in this work, experimental evidence for EDA interactions between carbenium ions and donors as well as between the counterions and acceptors were found. Since the counterions used are the same which one uses in cationic real systems, and the triphenylmethyl and tropylium cations should have an acceptor strength comparable with the cations derived from substituted styrenes, our conclusions on cationic real systems should be justified.

Scheme 3 represents the specific interactions between the solvent and the active species resulting from a solvent-separated ion-pair. The interaction with the monomer leads to an alteration of the solvation of the ion-pair, which should be expanded in the direction of the counterion. On the basis of a temporary dissymmetry of the sphere of solvation, stereoregularities or regularities of the structure of polymers may be explained. The velocity of this precoordinating EDA interaction as well as the "insertion" of the monomer into the ion-pair shows a different dependence on the stereoelectronic behavior
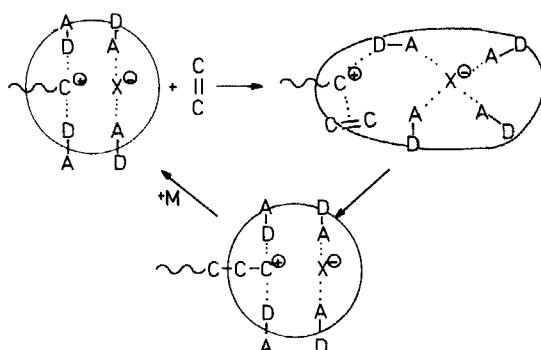
SCHEME 3. Ion-pair propagation reaction as competition be-
tween monomer-solvation (C=C) and specific solvent-solvation (A–D:
A is the acceptor part, D is the donor part).

of the electrophilic center, the solvent, as well as on the donor
strength of the monomer. With strong π-donors the formation of
radical ions by one electron transition in the CT complex must be
taken into account. After stabilization of the radical function, cationic
polymerizations may occur.

At present the competing EDA interactions among the electro-
philic center, the monomer, the solvent, as well as the counterion are
characterizable only in a qualitative manner, because the dissociation
degree of the active species or the temperature dependence of the
different EDA equilibria are unknown and their experimental separa-
tion is not yet settled. Using model systems with partial exclusion
of special interactions, the determination of cooperative parameters
characterizing the different EDA equilibria seems possible in prin-
ciple. This will be the aim of further investigations.

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