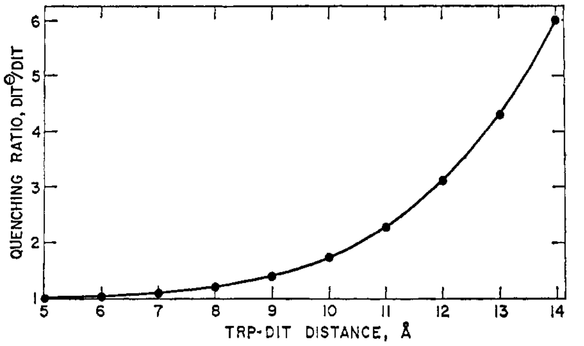

Figure 4. Efficiency of energy transfer from tryptophan (TRP) to ionized (DIT⁻) as compared to un-ionized (DIT) diiodotyrosine, as a function of the tryptophan–diiodotyrosine distance, calculated as described in text.

proteins can be estimated. These "averages" are strongly weighted in favor of the closest DIT residues, and do not at all include those DIT residues too far away to quench tryptophanyl fluorescence. These calculations assume that the distances between tryptophanyl and DIT residues do not change with increasing iodination or with DIT ionization. The structures of HSA and thyroglobulin, as examined by several criteria, are essentially unchanged by the levels of iodination in the preparations used here. Further, there are no major structural changes in either HSA or thyroglobulin in the pH range of DIT ionization.

The "average distance" between the DIT residues and the single tryptophanyl residue in HSA decreases slightly with increasing iodination. The average distance between the tryptophanyl residue and the first DIT residue formed is close to 10 Å. This value is close to the critical transfer distance of un-ionized DIT. Consequently a quenching of 50% of tryptophan emission is expected. The observed value is about 30% (Figure 1). At a distance of 10 Å, ionized DIT would be expected to quench tryptophan emission almost completely. Only about 55% quenching is observed (Figure 1). A value of K^2 of the orientation factor in the Forster equation less than $^2/_3$ could account for the low quenching efficiency, though other factors cannot be excluded. The distances calculated between tryptophan and DIT decrease from about 10 to 8.5 Å as the DIT content increases from 1 to 4 mol/mol of protein. It is clear that none of these residues can be within 8.5 Å of the tryptophan residue since tryptophan emission would be 80% quenched at this distance by a single residue. In addition all the residues must be within 16 Å or they would have negligible effect.

The distance between donor and acceptors in HSA is greatly increased in 8 *M* urea; in this solvent, there is no quenching of tryptophanyl fluorescence by un-ionized DIT residues. Thus, no DIT residues can be within several residues of the tryptophanyl residue along the polypeptide chain.

Steiner, *et al.*,[30] have recently studied the binding of thyroxine by HSA by the method of fluorescence quenching. HSA has one binding site with very high affinity for thyroxine; at pH 7.4, where the bound thyroxine is ionized, the binding constant is 1.6×10^6. The binding of 1 mol of thyroxine/mol quenches about 55% of the HSA fluorescence. This suggests that the strong thyroxine binding site is about 22 Å from the tryptophanyl residue in HSA.

The average distance between the tryptophanyl residues and the DIT residues in thyroglobulin does not change with increasing DIT content. This distance is about 8 Å in water, and only increases to about 9 Å in 9 *M* urea. Major structural elements persist in thyroglobulin in 9 *M* urea, as shown by fluorescence polarization measurements. These interactions are more completely eliminated in 6 *M* guanidine.[31] The failure to observe a large increase in the average distance may result from the close proximity of the large number of tryptophanyl and iodotyrosyl residues along the polypeptide chain, or from numerous clusters of residues which remain in 9 *M* urea.

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Communications to the Editor

Two Modes of Formation of Carbonium Ions from Olefins and Suitable Electron Acceptors

Sir:

Electron acceptors, *e.g.*, $SbCl_5$, convert polynuclear aromatic hydrocarbons into the respective radical cations which were identified by their esr[1] and optical[2] spectra. It has been claimed[3] that analogous electron-transfer processes produce radical cations from vinyl or vinylidene monomers and the latter initiate cationic polymerization. The initiation should resemble the anionic process;[4] radical cations are expected to dimerize into dicarbonium ions or to react with excess of monomer and yield dimeric radical cations.

To investigate the course of the initiation, we have chosen 1,1-diphenylethylene (D) as the "monomer." Its head-to-tail polymerization is prevented by steric hindrance, although the dimerization is feasible.[5] Hence, studies of the initiation in this system are not complicated by the subsequent polymerization.[5]

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Table I. Nmr Spectra of Carbonium Ions at −60°

Precursor	Solvent	Nmr, ppm[c] Ph_2C^+	$-CH_2C^+<$	$CH_3C^+<$	Integration ratio[d]
1,1-Diphenylethylene + $SbCl_5$	CH_2Cl_2	8.1 (m)	3.8 (s)		5.2 ± 0.3
	CD_2Cl_2	8.1 (m)	3.8 (s)		5.3 ± 0.4
	$CDCl_3$	8.1 (m)	3.8 (s)		5.4 ± 0.6
1,1-Diphenylethanol + $SbCl_5$	CH_2Cl_2	8.1 (m)		3.8 (s)	3.5 ± 0.4
	CD_2Cl_2	8.1 (m)		3.8 (s)	3.2 ± 0.3
	$CDCl_3$	8.1 (m)		3.8 (s)	3.3 ± 0.4
1,1-Diphenylpropanol + $SbCl_5$	$CDCl_3$	8.1 (m)	3.8 (q)		
1,1-Diphenylpropanol[a]	SbF_5, FSO_3H SO_2	8.0 (m)	3.7 (q)		
1,1-Diphenylethyl chloride[b]	SbF_5, FSO_3H	8.0 (m)		3.7 (s)	3.3

[a] G. A. Olah, M. B. Comisarow, C. A. Cupas, and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **87**, 2997 (1965). [b] G. A. Olah, *ibid.*, **86**, 932 (1964). [c] m, multiplet; s, singlet; q, quartet. Note the virtually identical chemical shift of the primary and secondary protons attached to carbon atoms adjacent to carbonium ion. This is shown by the spectra obtained from the 1,1-diphenylethanol and -propanol, both in our media and in Olah's. [d] Aromatic :aliphatic.

Using the technique described elsewhere,[6] a solution of D was allowed to react at −80° in methylene chloride with a precooled solution of $SbCl_5$ in the same solvent. The reaction was followed spectrophotometrically at low temperature. The first product (apparently charge-transfer complex) absorbs at λ_{max} 465 mμ, but within 15 min it has been converted into the final product absorbing at λ_{max} of about 435 and 310 mμ. The absorption in the 435- and 310-mμ region show a slight bathochromic shift at higher $SbCl_5$ concentration. The conversion appears to be quantitative if $SbCl_5$ is in large excess, *e.g.*, when $SbCl_5$:D = 5:1. On this basis the molar extinction coefficient at 435 mμ was calculated to be 30,000 per monomeric unit.

We anticipated the sequence of reactions given by eq 1 and 2.

$$D + SbCl_5 \rightleftarrows D{,}SbCl_5 \text{ (charge-transfer complex)} \rightleftarrows D\cdot^+{,}SbCl_5\cdot^- \quad (1)$$

$$2D\cdot^+{,}SbCl_5\cdot^- \longrightarrow SbCl_5\cdot^-{,}^+DD^+{,}SbCl_5\cdot^- \quad (2)$$

where $^+DD^+ = {}^+C(Ph)_2CH_2CH_2C^+(Ph)_2$. Indeed, the absorption at 435 and 310 mμ was shown to be due to the presence of the $-CH_2C^+(Ph)_2$ center. This conclusion is based on the following observations. (1) Under our conditions 1,1-diphenylethanol reacts with an excess of $SbCl_5$ and yields a species absorbing again at 435 and 310 mμ. Assuming quantitative absorption, ϵ_{435} is found to be 33,000. Quenching this solution at −70° with a methanol–water mixture (8:1 by volume) led to $CH_3C(Ph)_2OCH_3$ in 70–80% yield. Hence, the colored species was $CH_3C^+(Ph)_2,[SbCl_5OH]^-$. (2) The same procedure converts 1,1,4,4-tetraphenylbutane-1,4-diol into a species again absorbing at 440 (higher concentration of $SbCl_5$) and 313 mμ. At least a tenfold excess of $SbCl_5$ is needed for quantitative conversion, and the calculated ϵ_{440} was 30,000 per carbonium ion. Quenching with a methanol–water mixture (8:1 by volume) at −70° produced $(CH_3OC(Ph)_2CH_2)_2$ in 90% yield. Obviously, the colored species was $([SbCl_5,OH]^-,{}^+C(Ph)_2CH_2)_2$. (3) Olah reported[7] the formation of $CH_3C^+(Ph)_2$ and $CH_3CH_2C^+(Ph)_2$ carbonium ions in SbF_5–FSO_3H mixtures from the respective precursors (see Table I). The absorption was observed at λ_{max} 425 and 315 mμ (ϵ 37,000 and 28,000, respectively). The small changes in λ_{max}, when compared with our observations, are attributed to solvent and counterion effects.

Further identification of carbonium ions was achieved by nmr. The results are summarized in Table I and show that the primary and secondary protons adjacent to C^+ carbon have virtually identical chemical shifts. Hence, the distinction between $({}^+C(Ph)_2CH_2)_2$ and $C^+(Ph)_2CH_3$ is based on the integration ratio aromatic: aliphatic protons which should be 5.0 and 3.3, respectively. Thus the results given in Table I prove that the carbonium ions derived from D are not the products of protonation. Unfortunately, the extremely poor solubility of the diol at low temperatures made impractical the nmr studies of the respective dicarbonium ion. This dicarbonium ion was observed recently by Olah (private communication), the nmr spectrum of its CH_2 protons giving signals of δ 3.8 ppm.

To complete the identification of the colored species obtained from D, quenching experiments were performed. In spite of numerous attempts, quenching with the methanol–water mixture or with mixtures of methanol–liquid ammonia (2:1 by volume) did not yield a high proportion of the expected methoxy derivative. Apparently the counterion plays an important role in the quenching process. We were able to reproduce the experiments giving the high yield of the dimethoxy compound derived from the dicarbonium ions formed from the diol, while identical quenching of carbonium ions produced from D led to a mixture of about 10–12 compounds which were separated by thin layer chromatography. The effect of the counterion is noted in the different stabilities of the solution when prepared from D or from the diol. The former decomposes rapidly at −50° while the latter is relatively stable at this temperature.

The formation of the dicarbonium ion ($^+DD^+$) from D is demonstrated by the relatively high yield of 1,1,4,4-tetraphenylbutadiene formed in the course of quenching.[8] This product was isolated in 30–40% yield when a methanol–liquid ammonia mixture was used in quenching, and its identity was unequivocally proved by ir, nmr, and melting point. Small amounts of the dimethoxy derivative and only a trace of $CH_3C(Ph)_2OCH_3$ were formed and identified by the R_f value of the respective spots on the tlc plate.

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(8) The butadiene was isolated also in high yield from $^+DD^+$ derived from the diol when quenching conditions were slightly modified.

The most interesting product isolated from the mixture, when methanol–liquid ammonia was used as the quenching agent, was identified as $CH_3OC(Ph)_2CH_2SbCl_4(NH_3)$. It formed colorless crystals, mp 158–160°.

Anal.[9] Calcd: C, 36.6; H, 3.66; N, 2.85; Cl, 28.9; Sb, 24.7. Found: C, 35.9; H, 3.78; N, 3.56; Cl, 28.8; Sb, 25.9. The presence of methoxy and phenyl groups was demonstrated by ir. The nmr spectrum (in CF_3COCF_3–D_2O) showed phenyl protons at δ 7.2, CH_2 protons at δ 3.8, and OCH_3 protons at δ 2.9 ppm. The integration led to the expected ratio 10:2:3, respectively.

The antimony compound was allowed to react in $CDCl_3$ with $SbCl_5$ at $-60°$. The nmr spectrum of the solution showed two signals at δ 8.1 and 5.3 ppm. The former corresponds to aromatic protons of the Ph_2C^+– group (see Table I) and the latter is assigned to $>C^+CH_2SbCl_4$. It seems that the presence of the $SbCl_4$ group shifts the methylene protons further downfield from the position (3.7 or 3.8 ppm) observed in $(Ph_2C^+CH_2)_2$ or in $Ph_2C^+CH_2CH_3$.

The isolation of the antimony compound indicates that two routes lead to formation of carbonium ions from $SbCl_5$ and olefin. $SbCl_5$ may act as an electron acceptor, as shown by eq 1, or it may disproportionate,[10] as $2SbCl_5 \rightleftarrows SbCl_4^+,SbCl_6^-$. The addition of $SbCl_4^+$ to the olefin leads to the formation of the carbonium ion. This mode of carbonium ion formation from an olefin and an electron acceptor will be further elucidated in the following communication.[11]

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Formation of Carbonium Ions by Dissociative Electron Transfer

Sir:

Addition of tetranitromethane to 1,1-diphenylethylene in nitrobenzene (both components 1 *M*) produces instantaneously a new species, presumably a charge-transfer complex, which absorbs at λ_{max} 410 mμ. Assuming its extinction coefficient to be 10^3–10^4, its equilibrium concentration was estimated to be about 10^{-3}–10^{-2} *M*. Apparently the complex decomposes slowly, the spectrum broadens, and eventually a new peak develops at λ_{max} 385 mμ. This reaction is accelerated by daylight and seems to be completed in about 12 hr.

The final product was isolated in the form of yellow crystals, mp 85.5°. It was identified as 1,1-diphenyl-2-nitroethylene. *Anal.* Calcd for $C_{14}H_{11}NO_2$: C, 74.5; H, 4.89; N, 6.25. Found: C, 74.3; H, 4.9; N, 6.24. This compound was described earlier,[1] mp 86–87°. The nmr spectrum of our product shows a sharp singlet at δ 7.51 and an aromatic band at δ 7.1–7.48 ppm. Integration gives a 1:10 ratio. The 7.51 ppm singlet is attributed to the $>C{=}CHNO_2$ proton. This assignment is justified because the analogous hydrogen in 2,4-dimethoxy-β-nitrostyrene[2] absorbs at δ 7.7 ppm. The presence of the NO_2 group was confirmed by ir (1340 and 1540 cm^{-1}).

The nmr spectrum of 1,1-diphenylethylene gives two sharp singlets at δ 5.42 (olefinic proton) and 7.4 ppm (aromatic protons). Hence, the kinetics of formation of the nitro compound in deuterated nitrobenzene may be followed by observing the decay of the 5.42-ppm line. On this basis, it was found that the conversion reached 70% after 7 hr.

These observations suggest the following mechanism.

$$\mathrm{Ph_2C{=}CH_2 + C(NO_2)_4} \rightleftarrows \underset{\mathrm{I}}{\text{charge-transfer complex (rapid)}} \qquad (1)$$

$$\mathrm{I} \longrightarrow \mathrm{Ph_2C^+CH_2NO_2 + \bar{C}(NO_2)_3} \qquad (2)$$

$$\mathrm{Ph_2C^+CH_2NO_2 + \bar{C}(NO_2)_3 \longrightarrow Ph_2C{=}CHNO_2 + CH(NO_2)_3} \qquad (3)$$

Electron transfer to tetranitromethane results in dissociative capture.[3] Therefore, reactions 2 and 3 take place in a concerted manner, or the proton transfer takes place in the ion pair, and this accounts for the lack of dimerization.

To verify the existence of intermediate carbonium ion the reaction was reinvestigated in the presence of methanol. Under these conditions, as in the study of Schmidt, *et al.*,[4] the reaction yields the respective nitromethoxy derivative, *viz.*, $Ph_2C(OCH_3)CH_2NO_2$. This compound, previously described by Anschütz and Hilbert,[5] was isolated in nearly quantitative yield in the form of white crystals, mp 139.5°. *Anal.* Calcd for $C_{15}H_{15}NO_3$: C, 70.0; H, 5.81; N, 5.25. Found: C, 69.6; H, 5.9; N, 5.4. The nmr spectrum showed singlets at δ 7.8, 5.3, and 3.25 ppm in the ratio of about 10:2:3. Strong bands were seen in its ir spectrum, namely at 1555 and 1380 cm^{-1}, which characterize the aliphatic NO_2 or ONO groups,[6] and a less strong band at 1080 cm^{-1}, which indicates the presence of the C–O–R linkage. Since the compound is not solvolyzed when boiled with 97% formic acid,[7] it does not contain the ONO group.

It is obvious that the nitroethane derivative obtained in this experiment results from the carbonium ion $^+C(Ph)_2CH_2NO_2$. In the presence of methanol this ion is methoxylated and the proton from the hydroxyl group neutralizes the $^-C(NO_2)_3$ ion. In the absence of methanol the proton from the $>C^+CH_2NO_2$ group is transferred to $^-C(NO_2)_3$ and, therefore, the nitro olefin derivative is formed.

The proposed mechanism attributing the formation of the carbonium ion to the transfer of NO_2^+ group from tetranitromethane to olefin seems to be general.[8] This

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