On the Negative Species Formed in γ- or Ultraviolet-Irradiated Nonpolar Glasses

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As previously shown by several authors, negative species formed in photoionized or γ-irradiated solid solutions can be sensitively characterized by optically stimulating a neutralization luminescence. At least in nonpolar matrices, the neutralization luminescence excitation spectrum closely parallels the negative species absorption spectrum. For TMPD photoionized in 3MP or MCH, and pure γ-irradiated 3MP and MCH, three distinct negative species are thus characterized: (1) the matrix trapped electrons, among which glass relaxation effects permit us to distinguish type a and type b trapped electrons; (2) the TMPD anion, or a negatively charged TMPD photoproduct; and (3) a third species X^- observable only after large uv or γ-ray doses and electron ir bleaching. Since the solute photoionization is accompanied by the solvent sensitized dissociation, the species X^- can very likely be identified with $R \cdot {}^-_{solv}$, $R \cdot$ deriving from a hydrogen atom abstraction from the solvent molecule. The technique of neutralization luminescence stimulation permits us to differentiate $R \cdot {}^-_{solv}$ from $R \cdot_{solv}$ which have both an optical absorption in the same uv region.

Introduction

Delayed luminescence in organic glasses associated with γ irradiations or solute photoionization, either spontaneous or optically or thermally induced, has attracted considerable attention in recent years.

It has been noticed in particular that in nonpolar glasses such as 3-methylpentane (3MP) and methylcyclohexane (MCH), the excitation spectrum of the charge recombination luminescence closely parallels the matrix trapped electron and the solute anion absorption bands and may serve to identify the latter.[1]

In the particular case of N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD), widely used as a solute in photoionization experiments, TMPD⁻ formation has been assumed[2,3] but not conclusively characterized.[4] In the course of a recent study of TMPD and diphenyl-p-phenylenediamine (DPPD) photoionized in a methyltetrahydrofuran (MTHF) glass,[5] some extra bands present for TMPD and absent for DPPD have appeared in the stimulated luminescence spectrum.

The present report deals mostly with TMPD photoionized at 77 K in a MCH glass. Owing to the much higher glass viscosity the trapped electrons (e_t^-) thermal decay is significantly reduced compared to 3MP.[6]

For comparison, a few experiments on uv-irradiated TMPD–3MP systems and γ-irradiated MCH or 3MP glasses are also described.

Experimental Section

Degassed solutions of purified TMPD in MCH (4×10^{-3} M) in sealed Suprasil tubes are irradiated under λ 325 ± 50 nm with a high-pressure Hg arc (Osram HBO 500) and uv filter. The stimulated luminescence spectra are recorded with a Jobin Yvon "Bearn" spectrofluorometer equipped with a Sefram recorder and two additional filters. A red one which cuts λ <550 nm is placed at the exit of the excitation monochromator (exit slit 0.3 mm, $(\Delta\lambda/\lambda)_{max}$ = 4% at λ 850 nm). Another filter with a passing band λ 430 ± 80 nm is set in front of the analyzing monochromator (slit width 2 mm, $\Delta\lambda/\lambda$ = 10% at λ_{an}

480 nm). For uv stimulation the red filter is removed and the analyzing monochromator slit is set at 1.0 mm ($\Delta\lambda/\lambda$ = 2% for λ_{an} = 480 nm). Unless otherwise stated, all reported spectra are recorded 30 min after the end of the irradiation, when spontaneous isothermal luminescence has become negligible. The time required for scanning the entire spectrum is about 5 min. The recorded spectra are corrected for the e_t^- consumption under successive bleachings and for the variation with λ of the excitation light flux, the stimulated luminescence I_{SL} being itself linear with the bleaching light intensity.

The I_{SL} spectra viewed either at λ_{an} = 480 or 390 nm corresponding, respectively, to TMPD phosphorescence and fluorescence maximum, are the same. The results are reproducible within 15%.

Results and Discussion

1. Effect of Glass Relaxation. Typical neutralization luminescence excitation spectra for TMPD in MCH glass are presented in Figure 1. For presentation conveniences, we shall divide the spectrum into three regions, as shown.

Increasing the glass relaxation time Δt_1 between vitrification and irradiation is found to decrease the stimulated luminescence intensity I_{SL} in region 1—in agreement with previous observations[7]—and particularly in region 1a. For prolonged annealing at 77 K, the region 1a luminescence vanishes. As is well known, the I_{SL} also decreases when the delay Δt_2 between the irradiation and stimulation is increased due to spontaneous recombination of some of the photoelectrons. Δt_2 is found to affect 1a more than 1b. After taking account for the decrease of 1b which overlaps

(1) A. Déroulède, *J. Lumin.*, **3**, 302 (1971).
(2) J. B. Gallivan and W. H. Hamill, *J. Chem. Phys.*, **44**, 1279 (1966).
(3) A. Bernas, M. Gauthier, D. Grand, and D. Leonardi, *Int. J. Radiat. Phys. Chem.*, **1**, 229 (1969).
(4) A. Bernas and D. Grand, *J. Chim. Phys.*, **67**, 566 (1970).
(5) A. Bernas, D. Grand, and T. B. Truong, *J. Chem. Soc., Chem. Commun.*, 759 (1972).
(6) J. Lin, K. Tsuji, and F. Williams, *J. Amer. Chem. Soc.*, **90**, 2766 (1968).
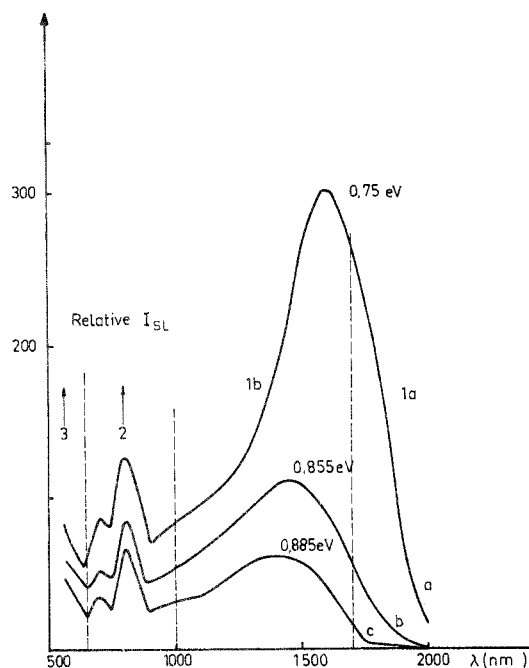(7) K. Funabashi, P. J. Herley, and M. Burton, *J. Chem. Phys.*, **43**, 3939 (1965).

Figure 1. Neutralization luminescence excitation spectrum for photoionized TMPD in MCH; effect of glass relaxation times Δt_1 and Δt_2; [TMPD] $= 4 \times 10^{-3}$ M, $T = 77$ K, dose 1.7×10^{20} photons cm^{-2}: curve a, $\Delta t_1 = 5$ min, $\Delta t_2 = 4$ min; curve b, $\Delta t_1 = 5$ min, $\Delta t_2 = 30$ min; curve c, $\Delta t_1 = 3$ hr, $\Delta t_2 = 30$ min.
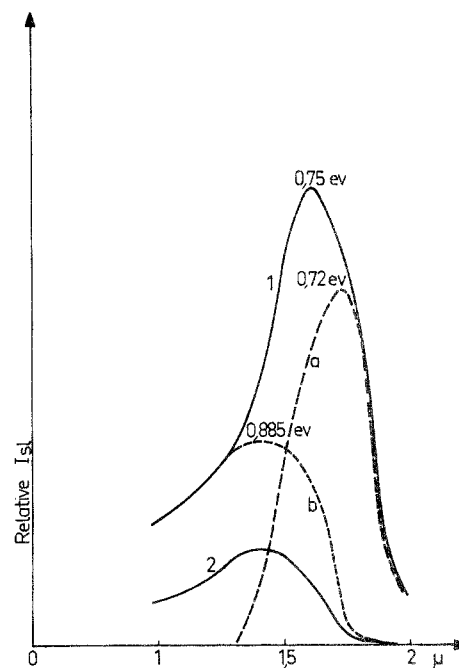

Figure 2. Decomposition of the e_t^- luminescence excitation band into 1a band (shallow traps) and 1b (deeper traps); [TMPD] $= 4 \times 10^{-3}$ M, $T = 77$ K; curve 1, $\Delta t_1 = 5$ min, $\Delta t_2 = 4$ min; curve 2, $\Delta t_1 = 3$ hr, $\Delta t_2 = 30$ min; curve b, curve 2 normalized at 1300 nm; curve a, difference between 1 and b.
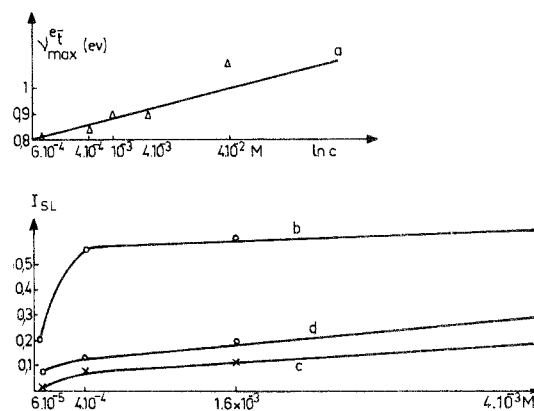
regions 2 and 3, it is found that the latter are not affected by Δt_1 or Δt_2. The influence of Δt_1 and Δt_2 is illustrated by curves c and b of Figure 1. The rate of sample vitrification also intervenes: for slower vitrification the 1a luminescence is weaker.

These observations, along with reported results in the literature[7-9] support the existence in 3MP and MCH glasses of "physical" or "intermolecular" electron traps more or less permanent and deep. The influence of Δt_2 and Δt_1 allows a decomposition of the e_t^- band into 1a and 1b bands with λ_{max} at 0.72 and 0.88 eV, respectively (Figure 2). To our knowledge, the 1a and 1b trapped electrons have not been discriminated before.

The transient traps 1a, created by rapid cooling, progressively disappear as the glass relaxes. Once bleached off, these shallow traps cannot be repopulated by subsequent bleaching in region 2. The more permanent and deeper traps 1b, as we shall see later, can be partially refilled by bleaching in region 2 or 3.

The ν_{max} of the e_t^- band is found to be shifted toward the blue ($\Delta\nu_{max} \simeq 0.15$ eV) as Δt_2 increases. For TMPD in 3MP, slight differences are observed: the effects of Δt_1 and Δt_2 are more pronounced but, whatever their duration, the shallow traps 1a are always present.

For both matrices, it must be concluded that the trapping centers undergo molecular reorganization not only on a microseconds scale[10] but over periods of hours.

2. Effect of Dose. The areas under the region 1 and 2 bands, respectively, are found to increase and then decrease with increasing uv irradiation time, whereas the luminescence intensity in region 3 is found to increase regularly with dose. The same trends have been reported for the e_t^- absorption band and the optical density in spectral region 3 for γ-irradiated MCH and 3MP glasses.[11,12]

As remarked elsewhere,[5] the ν_{max} of the e_t^- band is shifted towards the blue as the dose increases, for uv or γ irradiations. It may be noted that the ν_{max} shift with in-

Figure 3. Effect of TMPD concentration c on ν_{max} of the e_t^- band and on the luminescence intensities I_{SL} in region 1 (e_t^-) and in region 2 (A$^-$), respectively; curve a, $\nu_{max}{}^{e_t^-}$ vs. ln c; curve b, area under e_t^- band vs. c; curve c, area under A$^-$ bands vs. c; curve d, ratio A$^-$ bands area/e_t^- band area vs. c.

creasing dose ($\Delta\nu_{max} \simeq 0.15$ eV) is the same as the ν_{max} shift following glass relaxation (Figure 2).

3. Effect of Solute Concentration. The areas of the I_{SL} bands in region 1 (curve b, Figure 3) and in region 2 (curve c, Figure 3) increase with solute concentration c from 6×10^{-5} to 4×10^{-3} M. For higher concentrations, the glasses become opaque and the experiments become less conclusive.

The ratio of the integrated intensities I_{SL} in region 2 to I_{SL} in region 1 is found to increase with c (curve d, Figure 3).

There is also a blue shift of ν_{max} of the e_t^- band with

(8) O. Janssen and K. Funabashi, *J. Chem. Phys.,* **46,** 101 (1967).
(9) B. Wiseall and J. E. Willard, *J. Chem. Phys.,* **46,** 4387 (1967).
(10) J. T. Richards and J. K. Thomas, *Chem. Phys. Lett.,* **8,** 13 (1971).
(11) M. Shirom and J. E. Willard, *J. Amer. Chem. Soc.,* **90,** 2184 (1968).
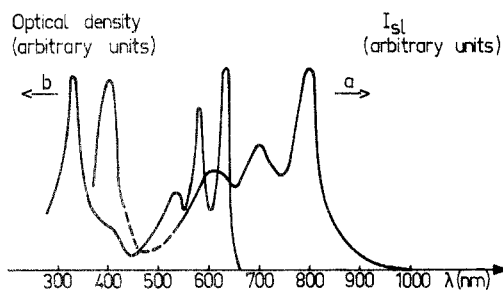(12) A. Eckstrom, R. Suenram, and J. E. Willard, *J. Phys. Chem.,* **74,** 1888 (1970).

Optical density
(arbitrary units)

I_{sl}
(arbitrary units)

Figure 4. TMPD$^-$ luminescence excitation spectrum (a). compared to TMPD$^+$ absorption spectrum (b) in 3MP glass at 77K (in the range ~430–550 nm, luminescence recording is not possible due to bleaching light scattering).
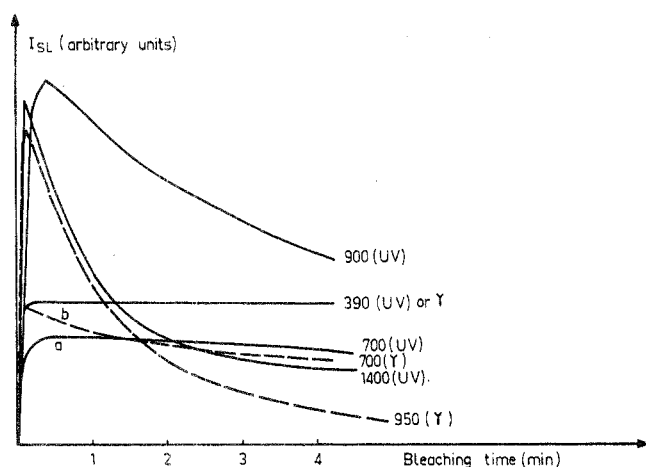
I_{SL} (arbitrary units)

Figure 5. I_{SL} decay curves for photoionized TMPD in MCH or γ-irradiated MCH bleached under various bleaching wavelengths (λ_b).

I_{SL} (arbitrary units)

Figure 6. I_{SL} of γ-irradiated 3MP glass in spectral region 3, i.e., X$^-$ region: curve a, 2-min ir stimulation, dose 1.1×10^{20} eV g^{-1}; curve b, 30-min ir stimulation, dose 1.1×10^{20} eV g^{-1}; curve c, 30-min ir stimulation, dose 4×10^{20} eV g^{-1}.

increasing c: $\nu_{max} = a \log c$ + constant (curve a, Figure 3).

Extrapolation to $c = 0$ gives $\nu_{max} = 0.8$ eV, which is the approximate value we have found for pure γ-irradiated MCH at low doses.[5]

4. Effect of Selective Bleachings. a. When $\lambda_b = 2000$ nm, the 1a band can be removed whereas the 1b band decreases in intensity but cannot be totally suppressed. For $1700 > \lambda_b > 1500$ nm, 1a and 1b can both be removed; band 2 is unchanged in MCH but increases for TMPD–3MP systems; band 3 intensity increases in MCH and 3MP after high uv or γ-ray doses.

b. After a short uv irradiation ($t = 1$ min in our experimental conditions), a sample which has been completely bleached off with ir light, then subsequently excited with λ_b comprised between 950 and 580 nm will partially recover the 1b e_t^- band. The 1a band in MCH, once bleached off, will never be restored. For higher uv doses, band 3 increases in intensity in MCH and 3MP. Analogous regenerating of the ir e_t^- spectrum by excitation in a solute anion band and electron transfer from one type of trap to another have been previously depicted for γ-irradiated systems.[2,12,13] Similar observation has also been made for TMPD photoionized in 3MP bleached first in the ir and then in the near-uv (360 to 400 nm).[14] The possible regeneration of the e_t^- band, together with the increase of I_{SL} in region 2 with increasing solute concentration, the presence of similar stimulated luminescence bands for TMPD photoionized in MTHF, and their absence in DPPD–MTHF system[5] or in pure γ-irradiated MCH and 3MP seem to demonstrate the existence of TMPD$^-$ or of a ne-
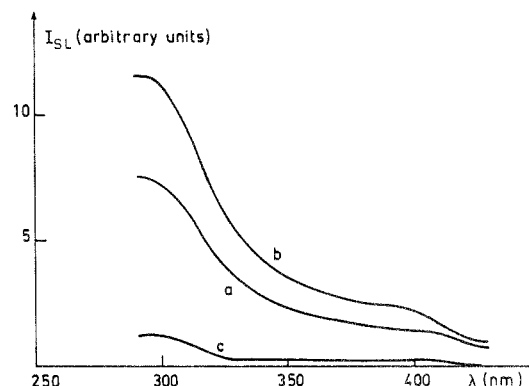
gatively charged TMPD photoproduct. The related luminescence excitation spectrum appears very similar to the well-known TMPD$^+$ absorption spectrum (Figure 4).

The existence of traps of two different natures is also confirmed by the observation of quite different luminescence decay curves accompanying bleachings in regions 1 and 2, respectively (Figure 5). One should particularly notice the dissimilarity between curve a (in which case the 700-nm bleaching affects TMPD$^-$) and curve b (in which case the 700-nm bleaching affects e_t^-).] On the time scale used, the number of charges undergoing neutralization per unit time upon visible excitation attain a nearly stationary state. Similar luminescence signals have been recently reported for γ-irradiated 3MP glasses.[15]

c. After large uv doses, for $650 < \lambda_b < 550$ nm, the 1b and 2 bands (which have been optically bleached off) are partially recovered for the photoionized TMPD in MCH or 3MP glass.

d. In region 3 the TMPD$^-$ luminescence excitation spectrum overlaps that of another species X$^-$. The contribution of the latter increases steadily with dose whereas that of TMPD$^-$ first increases and then declines.

For a pure, γ-irradiated (1×10^{20} eV g^{-1}) MCH or 3MP sample, the following preliminary observations have been made. (1) If the stimulation occurs immediately after the irradiation, the excitation spectrum attributable to X$^-$ is absent. (2) Following a 1400-nm bleaching, the stimulated luminescence becomes observable in region 3. Its intensity increases with the ir 1400-nm bleaching time (Figure 6) as was observed through absorption measurements.[12] (3) If the 1400-nm bleaching is followed by a 380-nm bleaching, the e_t^- band is partially regenerated, which shows that a 380-nm light can photodetach the electron from X$^-$. (4) After a prolonged glass relaxation Δt_2, no X$^-$ excitation spectrum is obtained, which is compatible with the generally adopted view that, during Δt_2, the shallowest, that is, the electrons trapped the nearest their parent cations, suffer neutralization; for such e_t^-, attachment to a X species would not compete with neutralization. (5) After high γ-ray doses (4×10^{20} eV g^{-1}) corresponding to a negligible concentration of e_t^-,[11,12] in either MCH or 3MP samples, a weak I_{SL} in re-

(13) A. Déroulède, F. Kieffer, and M. Magat, *Advan. Chem. Ser.*, **No. 82**, 401 (1968).
(14) W. M. McClain and A. C. Albrecht, *J. Chem. Phys.*, **43**, 468 (1965).
(15) K. Funabashi, C. Hebert, and J. L. Magee, *J. Phys. Chem.*, **75**, 3221 (1971).

gion 3 is observed only after an ir stimulation (curve c, Figure 6).

The nature of the uv absorbing species X^- has already been the subject of some debate.[12,15] Previous studies and the present one agree that X^- is observable only after heavy radiation doses and derives from the solvent.

The uv absorption[15] or stimulated emission band cannot be a second e_t^- (β) band since its intensity varies in opposite direction from the ir trapped electron band. It does not seem to be correlated with a dielectron formation which would give rise to an absorption at longer wavelength than e_t^-.[16]

It has been suggested that X is very likely a solvent radical although a decrease in [$R\cdot$] following an e_t^- bleaching and $R\cdot^-$ formation has not been recorded through epr spectroscopy.[11,17]

For the uv-irradiated systems, it has been repeatedly shown[18-22] that solute photoionization is accompanied by a solvent-sensitized dissociation, leading to $R\cdot$ + H whenever the solvent molecules contain mobile hydrogen atoms. Quantitatively it has been estimated that the ratio solute cation/solvent radical is of the order of one for 3MP.[23]

Hence, our photochemical results seem to support the identification of X^- with $R\cdot^-_{solv}$; $R\cdot$ deriving from a H-atom loss by the solvent molecule. We should also point out that a dissociative electron capture by 3MP or MCH molecules is not feasible on energetic grounds.

The last point which deserves emphasis is that the incoming, thermalized electrons do not seem to attach to $R\cdot$; it is only after having been trapped and optically (not thermally) released, that mobile electrons appear capable of producing $R\cdot^-$. Similar results have been previously reported for γ-irradiated acetonitrile in glassy MTHF.[24] One may tentatively offer two suggestions. (a) The electron capture would be of a resonant type and the bleaching electron with 0.15–0.12-eV kinetic energy[5] would encounter radicals stabilized in the immediate vicinity of the electron-trapping cavities. (b) The bleaching light would serve not only to release the trapped electrons but also to induce some C–H vibrational excitation in the radical, thereby increasing the electron capture cross section.

Further experiments are in progress to test these tentative interpretations.

(16) A. Eckstrom, *Rad. Res. Rev.*, **2**, 381 (1970).
(17) D. P. Lin and L. Kevan, *J. Chem. Phys.*, **55**, 2629 (1971).
(18) B. Smaller, *Nature (London)*, **195**, 593 (1962).
(19) B. N. Shelimov, N. V. Fok, and V. V. Voevodsky, *Dokl. Akad. Nauk SSSR*, **144**, 596 (1962), V. G. Vinogradova, *et al.*, *ibid.*, **154**, 188 (1964).
(20) Kh. S. Bagdassarian, *et al.*, *Dokl. Akad. Nauk SSSR*, **152**, 349 (1963); **153**, 374 (1963); **160**, 625 (1965).
(21) S. Siegel and K. Eisenthal, *J. Chem. Phys.*, **42**, 2494 (1965).
(22) B. Brocklehurst, *et al.*, *Trans. Faraday Soc.*, **62**, 1793 (1966).
(23) M. C. Peraudeau, Thèse 3ème cycle, Paris, 1970; A. Bernas, *et al.*, 5th International Conference on Photochemistry, New York, N. Y., Sept 1969.
(24) M. A. Bonin, J. Lin, K. Tsuji, and F. Williams, *Advan. Chem. Ser.*, **No. 82**, 269 (1968).

Pulse Radiolysis of Solutions of Stilbene. I. Evidence for Triplet and Singlet Excited State Formation

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The triplet state of *trans*-stilbene has been estimated, both by direct observation and by an energy transfer method, to have a natural first-order decay constant, $k = 1.06 \pm 0.26 \times 10^7$ sec^{-1}, in benzene solution. This species can transfer triplet energy to anthracene with a second-order rate constant, $k = 2.6 \pm 0.5 \times 10^9$ M^{-1} sec^{-1}. Other energy transfer processes involving the cis and trans isomers of stilbene have been investigated.

Introduction

Extensive studies of the direct and photosensitized isomerization of stilbene in solution[1-4] have led to the conclusion that the active intermediate is the triplet state of stilbene. The observed photostationary state[3] of isomeric composition [cis]/[trans] = 1.8 agrees with theoretical calculations[5] of the first excited triplet energy surface.

Studies of the radiation-induced isomerization of stilbene in benzene and cyclohexane[6,7] led to the observation of a radiostationary state in dilute solutions similar to

that of the photoreaction. This fact combined with the ef-

(1) S. Malkin and E. Fischer, *J. Phys. Chem.*, **66**, 2482 (1962).
(2) R. H. Dyck and D. S. McClure, *J. Phys. Chem.*, **36**, 2326 (1962).
(3) S. Malkin and E. Fischer, *J. Phys. Chem.*, **68**, 1153 (1964).
(4) G. S. Hammond, *et al.*, *J. Amer. Chem. Soc.*, **86**, 3197 (1964).
(5) P. Borrell and H. H. Greenwood, *Proc. Roy. Soc., Ser. A*, **298**, 453 (1967).
(6) E. Fischer, H. P. Lehmann, and G. Stein, *J. Chem. Phys.*, **45**, 3905 (1966).
(7) R. R. Hentz, D. B. Peterson, S. B. Srivastava, H. A. Barzynski, and M. Burton, *J. Phys. Chem.*, **70**, 2362 (1966).