Fig. 1.—Solvolysis of copolymer I (6.14 M in ester groups): $-O-$, without catalyst; $-\bullet-$, with 0.02 M N-methylimidazole; $-\triangle-$, with 2.5 $\times$ 10^{-5} M (concentration expressed in imidazole units) poly(N-vinylimidazole); $-\nabla-$, with 5 $\times$ 10^{-4} M poly-(N-vinylimidazole); $-\blacktriangle-$, with 0.02 M poly(N-vinylimidazole). Solid lines, read bottom time scale; broken lines, read top time scale.

duced. The polymeric catalyst–substrate system is particularly favorable for demonstrating these phenomena since the individual substrate molecules possess numerous anionic sites that are attracted by the multiple cationic sites on the catalyst.

In support of the concept that reversible association between catalyst and substrate is involved in these reactions it was found that poly(acrylic acid), which competes with the copolymer for binding sites on poly-(N-vinylimidazole), functioned as an inhibitor in the catalyzed solvolyses (Table I).

TABLE I[a]

Poly(acrylic acid) (moles/l. of ester groups)	$10^3 k'$, min.$^{-1}$
0	65
5 $\times$ 10^{-4}	28[b]
10 $\times$ 10^{-4}	14[b]

[a] Copolymer I, 6.4 $\times$ 10^{-5} M in ester groups; poly(N-vinylimidazole), 5 $\times$ 10^{-4} M in imidazole units. [b] k' decreased somewhat as the reaction progressed. These values correspond to the first 30% of the reaction.

TABLE II

Catalyst	$10^3 k$, min.$^{-1}$ (dinitrophenyl isopropylbenzoate)	$10^3 k$, min.$^{-1}$ (copolymer I)
None	2.2	1.54
N-Methylimidazole (2 $\times$ 10^{-2} M)	56.5	33.
Polyvinylimidazole (5 $\times$ 10^{-4} M in imidazole units)	3.1	65

Data demonstrating selective solvolysis of a pair of substituted dinitrophenyl benzoates are given in Table II. With N-methylimidazole as catalyst 2,4-dinitro-
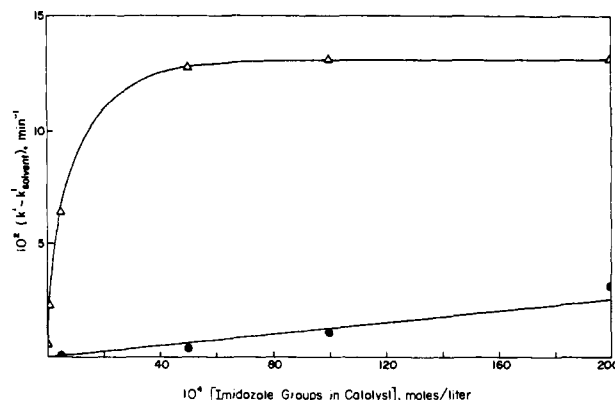

Fig. 2.—Solvolysis of copolymer I (6.14 $\times$ 10^{-4} M in ester groups) catalyzed by poly(N-vinylimidazole) ($-\triangle-$), 2.5 $\times$ 10^{-5}—2 $\times$ 10^{-2} M in imidazole groups, and by N-methylimidazole ($-\bullet-$), 5 $\times$ 10^{-4}—2 $\times$ 10^{-2} M.
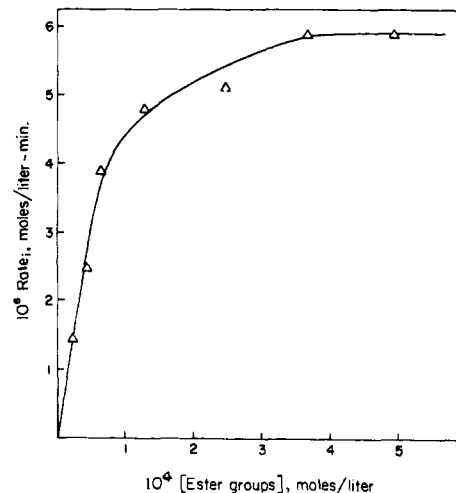

Fig. 3.—Solvolysis of copolymer I, catalyzed by poly(N-vinyl-imidazole, 5 $\times$ 10^{-4} M.

phenyl p-isopropylbenzoate solvolyzed somewhat faster than copolymer I. On changing the catalyst to poly(N-vinylimidazole) it was found that copolymer I solvolyzed markedly faster than dinitrophenyl p-isopropylbenzoate. Selectivity results from *acceleration* in the rate of solvolysis of the substrate capable of binding to the catalyst.

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The Effect of Electrolytes on Circular Dichroism Curves of [Co(en)₃]Cl₃

Sir:

It is well known that the observed optical rotation of optically active complexes depends upon the optically inactive ions present as charge compensators. Some previous studies of this effect have been carried out either at a fixed concentration of inactive ion,[1] or at only one wave length.[2] Tsuchida[3] has reported that the maximum in the optical rotatory dispersion (ORD)

(1) M. J. Albinak, D. C. Bhatnagar, S. Kirschner, and A. J. Sonnessa, Can. J. Chem., 39, 2360 (1961).
(2) R. Larsson, Acta Chem. Scand., 16, 2267 (1962).
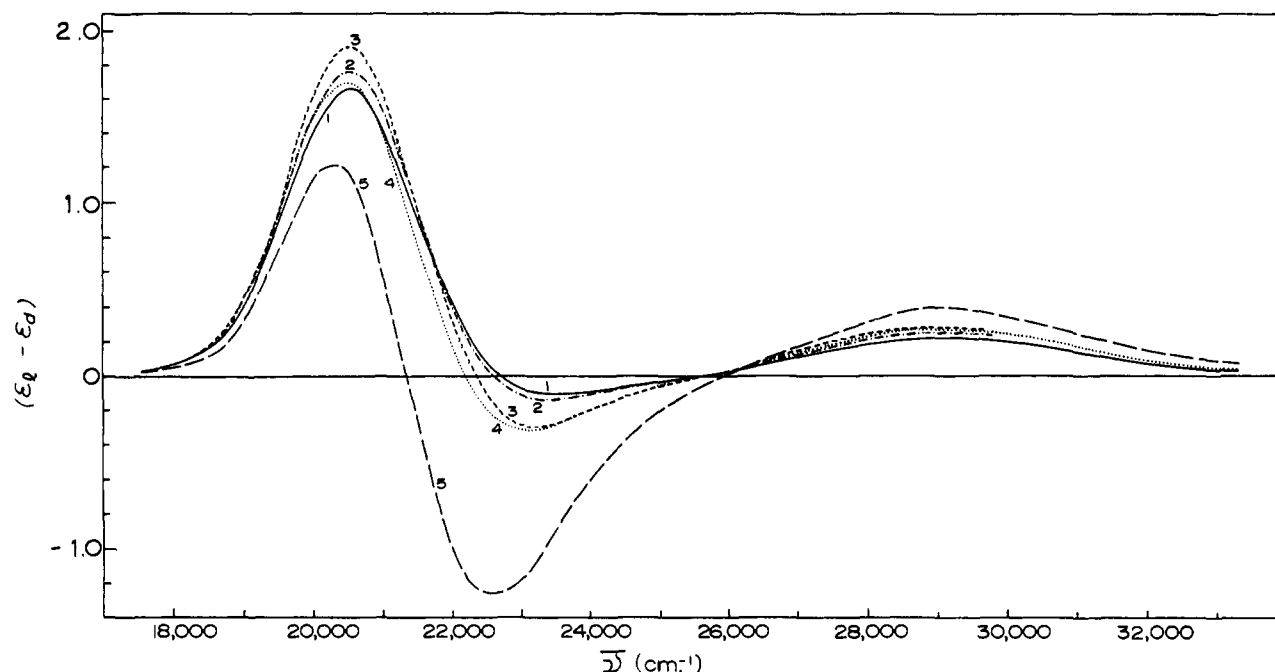(3) R. Tsuchida, J. Chem. Soc. Japan, Pure Chem. Sect., 58, 621 (1937).

Fig. 1.—Effects of electrolytes on the circular dichroism curve of 1.6×10^{-3} M [Co(en)$_3$]Cl$_3$ containing: (1) no additional electrolyte, (2) 0.5 M NaCl, (3) 3.0 M NaOH, (4) 0.5 M Na$_2$SO$_4$, and (5) 0.5 M Na$_3$PO$_4$.

curve of (+)-[Co(en)$_3$]Br$_3$ is shifted toward shorter wave length on addition of KBr until a 1:1 mole ratio is reached. The peak shifts back toward the original concentration for higher proportions of KBr. This communication reports results of a study of the effects of electrolytes on the circular dichroism (CD) of (+)$_{546}$-[Co(en)$_3$]Cl$_3$·H$_2$O (en = ethylenediamine). The individual components of CD spectra are more easily separated than those of ORD or absorption spectra.[4] This makes the interpretation of CD spectra much easier and it permits the effect of electrolytes on individual components to be examined. These effects cannot be seen from ORD or absorption spectra.

The CD measurements were made as follows. The desired electrolyte was dissolved in water, added to a measured volume of a stock solution of (+)$_{546}$-[Co(en)$_3$]Cl$_3$, and diluted to a volume so that the solution was 1.6×10^{-3} M with respect to the complex and contained the desired molarity of the electrolyte. The CD curves were obtained on a Jouan dichrograph using 5-cm. Beckman cells. Typical results are shown in Fig. 1.

Several gross changes are observed in the CD spectra on addition of a large excess of electrolyte. With the exception of Na$_3$PO$_4$, the electrolytes increase the intensity of all CD peaks, but not to the same extent for all electrolytes or for all peaks. The low energy positive peak (^{1}A → ^{1}E$_a$) shows a small increase for sodium salts of Cl$^-$, OH$^-$, and SO$_4^{2-}$ ions, while this peak decreases in intensity in the presence of Na$_3$PO$_4$. The negative CD peak (^{1}A → ^{1}A$_2$) increases in intensity for all of the electrolytes, with the PO$_4^{3-}$ ion having a much greater effect than the other anions. It is possible that the very large effect of PO$_4^{3-}$ on the ^{1}A$_2$ peak may pull down the ^{1}E$_a$ peak, masking the real effect of PO$_4^{3-}$ on the latter peak. The effects on the second positive CD peak are very small for all electrolytes except Na$_3$PO$_4$.

The data presented were chosen to show the comparison of anions at constant molarity (except for NaOH). The effects of different electrolytes reach saturation levels at different concentrations. For Cl$^-$ the effect increases to a maximum at 2 M NaCl. The maximum effect of OH$^-$ is that shown (3 M NaOH). The effect of the OH$^-$ ion is about the same as that of other univalent anions of the same concentration, and hence there are no large pH effects which might confuse the effect of PO$_4^{3-}$. The curve for PO$_4^{3-}$ represents the limiting effect with this ion. The effect with 0.05 M Na$_3$PO$_4$ was almost as great.

For the negative peak, the SO$_4^{2-}$ ion has an effect which is intermediate between that of univalent ions (of the same concentration) and the PO$_4^{3-}$ ion. The same order is not observed for the low energy ^{1}E$_a$ peak, although the serious overlap of these two peaks could cause irregularities.

Work is in progress to determine to what extent the different factors play a role in the over-all changes in CD data with complexes of different charge types. It is apparent that the effects of electrolytes can be greatly confused from ORD or absorption spectra where the individual components are not separated. The investigation of "outer sphere" complexes from such data can give false impressions of even the order of stabilities of the complexes. The interpretation of the relative intensities of the ^{1}A$_2$ and ^{1}E$_a$ components of [Co(en)$_3$]Cl$_3$ in solution and in solid 2[(+)-Co(en)$_3$-Cl$_3$]·NaCl·6H$_2$O by McCaffery and Mason[5] is also questionable in light of the expected great effect of the Cl$^-$ ions in the crystal lattice.

This technique has been demonstrated as an aid in interpreting CD spectra by the enhancement of weak bands by the addition of an electrolyte to the solution of optically active [Co(en)$_2$gly]I$_2$.[6]

The relative effects of the anions are not the same as expected from the association constants determined for

(4) B. E. Douglas, R. A. Haines, and J. G. Brushmiller, *Inorg. Chem.*, **2**, 1194 (1963).

(5) A. J. McCaffery and S. F. Mason, *Mol. Phys.*, **6**, 359 (1963).
(6) C. T. Liu and B. E. Douglas, *Inorg. Chem.*, **3**, 1356 (1964).

[Co(en)₃]³⁺ with OH⁻, Cl⁻, and SO₄²⁻ by an independent method.[7] However, it should be noted that spectrochemical effects need not necessarily be in the same order as thermodynamic association constants, and, of course, the effects of the different electrolytes are not the same for the two CD bands.

(7) D. R. Stranks, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., Macmillan Co., New York, N.Y., 1961, p 574.

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Radiolysis in the Adsorbed State[1]

Sir:

Studies of the decomposition by γ-rays of molecules adsorbed on chemically inert mineral supports[2-6] have shown that excitation energy delivered to the solid from the radiation can migrate to the surface and become available for decomposition of the adsorbate. For a further study of this process, we have selected azoethane, $(C_2H_5)_2N_2$, as adsorbate, since the chief decomposition product, nitrogen, is readily separated and measured. Minor gaseous products, hydrogen and methane, which separate with the nitrogen and are measured simultaneously, serve as indicators of the occurrence of other modes of decomposition which presumably require more energy than needed for the production of nitrogen. Radiolysis of pure liquid azoethane gave $G(N_2) = 3.69$, $G(H_2) = 0.46$, and $G(CH_4) = 0.076$.

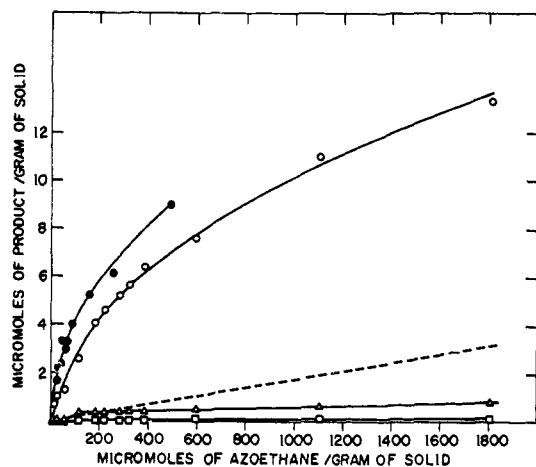

Fig. 1.—Radiolysis products of azoethane adsorbed on silica gel, Co⁶⁰ γ-rays, dose 5.9 Mrads: open symbols, Fisher Scientific Co. gel, surface 775 m.²/g. determined by the B.E.T. method using N₂; solid symbols, gel heated to 800° in air for 16 hr., surface 500 m.²/g.; circles, N₂; triangles, H₂; squares, CH₄; dotted line is "expected" nitrogen yield (see text).

When adsorbed on silica gel and radiolyzed (Fig. 1), azoethane behaved much like pentane.[2,3] As the amount of azoethane on the gel was increased, the amount of product formed increased, very rapidly at first, more slowly at higher coverages. The dotted

(1) Research performed under the auspices of the U. S. Atomic Energy Commission.
(2) J. M. Caffrey, Jr., and A. O. Allen, *J. Phys. Chem.*, **62**, 33 (1958).
(3) J. W. Sutherland and A. O. Allen, *ibid.*, **64**, 1040 (1960).
(4) R. Coekelbergs, A. Crucq, A. Frennet, J. Decot, and L. Timmerman, *J. chim. phys.*, **60**, 51 (1963).
(5) R. R. Hentz, *J. Phys. Chem.*, **66**, 1625 (1962).
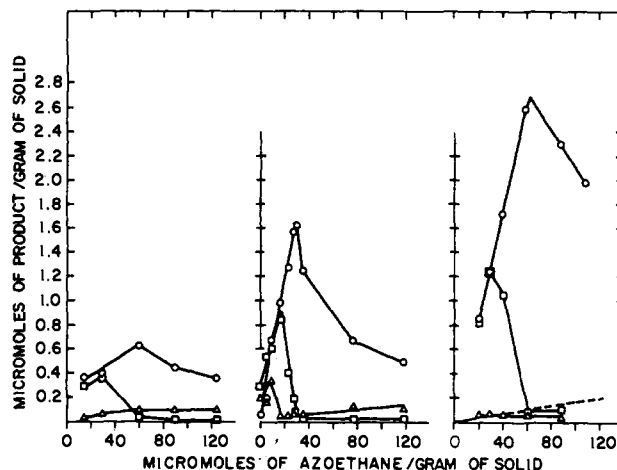(6) W. H. Clingman, Jr., *Ind. Eng. Chem.*, **52**, 72 (1960).

Fig. 2.—Radiolysis products of azoethane adsorbed on magnesium oxide, Co⁶⁰ γ-rays, dose 5.9 Mrads: left, oxide prepared by heating basic carbonate in air for 16 hr. to 600°; center, to 800°; right, to 1140° (meaning of symbols as in Fig. 1).

"liquid line" shown in the figures represents the amount of nitrogen that would be formed if only the energy absorbed by the azoethane were effective in decomposing it and the yield of nitrogen were the same as for the liquid. That the actual yield of nitrogen is many times greater than that shown by the liquid line indicates transfer of energy from the solid. An interesting observation was made during the blank runs. Silica gel irradiated to 6 Mrads under vacuum turns blue. Simply on exposure to azoethane vapor, the blue color immediately disappeared, while nitrogen was evolved to the extent of about 10% of what would have formed if the azoethane had been present during the irradiation. Similar observations are reported by Kohn and by Hentz.[7] That practically all the color centers interact with the added material seems less surprising if we remember that, in silica gel, practically all the solid lies within two atomic diameters of the surface.

With magnesium oxide the results were more unexpected (Fig. 2). Three preparations were heated to different temperatures. Surface determination of the two higher temperature preparations, by the B.E.T. method using nitrogen, gave 29 m.²/g. for both. It is known, however,[8] that the higher calcination temperature yields an oxide of less imperfect crystalline structure and lower energy. Figure 2 shows that, at low coverages, extensive energy transfer to azoethane occurs, the efficiency being greater the more perfect the crystal lattice. Most striking, however, is the decline at higher coverages of the total amount of decomposition. Thus additional azoethane not only fails to decompose but protects the first molecules adsorbed against decomposition. The amount of azoethane required for maximum yield is quite different for the different gaseous products, being higher for nitrogen than for methane. Hydrogen exhibited a maximum at a still lower amount of azoethane for the sample of magnesium oxide prepared at 800°. The decline sets in well below complete monolayer coverage, which should occur at around 120 μmoles/g. if the area per adsorbed azoethane molecule is assumed

(7) (a) H. W. Kohn, *Nature*, **184**, 630 (1959); (b) R. R. Hentz, *J. Phys. Chem.*, **66**, 2714 (1962).
(8) R. Fricke and J. Lueke, *Z. Elektrochem.*, **41**, 174 (1935); R. M. Dell and S. W. Weller, *Trans. Faraday Soc.*, **55**, 2203 (1959).