Supplementary Material Available: Crystallographic details for **4a**·$(C_2H_5OH)_2$, including tables of atomic coordinates, thermal parameters, bond lengths, and bond angles (10 pages); structure factor amplitude table for **4a**·$(C_2H_5OH)_2$ (17 pages). Ordering information is given on any current masthead page.

Direct Observation of Association Processes between Polymer Latex Particles

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Received October 29, 1986

The study of association–dissociation processes between solute species has in most cases been carried out by measuring the changes of parameters associated with the physical processes. One of the widely used techniques is spectrophotometry. In this paper, we report briefly on a kinetic investigation of two association processes of polymer latex particles with the use of a much more direct technique. We have taken advantage of latex particles being large enough to be observed by the naked eye with an ultramicroscope. To our knowledge this is the first "direct" determination of kinetic parameters. The first system studied here is the association reaction between oppositely and highly charged latex particles, and the second one is the selective association reaction between almost neutral latex particles carrying antigen and those carrying antibody on their surfaces.

An aqueous suspension of anionic latex particle G-5301 (poly(styrenesulfonic acid-*co*-styrene), diameter 3700 Å, charge density 10 μC·cm^{-2}, final concentration 8.1×10^{-12} M[1], based on particles) obtained from Japan Synthetic Rubber Co. was mixed with a 10 times excess amount of a suspension of cationic latex particles MATA-2 synthesized by us (poly(3-methacryloylaminopropyltrimethylammonium chloride-*co*-styrene), diameter 3000 Å, charge density 4.0 μC·cm^{-2}) in a thermostated observation cell set on a microscope (Carl Zeiss AXIOMAT, IAC). Both latices were monodispersed according to electron microscopy, and their suspensions were purified beforehand by thorough washing with mixed-bed ion-exchange resin (Amberlite MB-3) and an ultrafiltration method. The mixing was completed rapidly by using a polyethylene mixing rod, the association process was recorded on a video tape recorder, and the information was transferred onto a video disk. By replaying the video disk, the percents of dimeric particles in the suspension mixture were evaluated at appropriate intervals by using an image data analyzer (Carl Zeiss IBAS).[2] The number of particles in the visual field is large enough (>250) for statistical calculation.

Since the association in water was too fast for the microscopic observation, we carried out the study in 30% (w/v) aqueous sucrose solutions at 25 °C. Only dimeric and monomeric particles (no higher aggregates) were observed during the association (within 20 min after mixing). The time dependence of the percents of the dimeric particles in the reacting suspension are shown in Figure 1. Using the number of dimeric particles in the suspension calculated from this figure, we could obtain the reciprocal of the relaxation time of the association of the latex particles of opposite charges as 9.1×10^{-3} s^{-1}, which is nearly equal to the first-order rate constant because the backward process was hardly perceptible, and therefrom the second-order rate constant of this association reaction was calculated to be 1.1×10^8 M^{-1} s^{-1}. This suggests that the association reaction of oppositely charged latex particles is almost diffusion-controlled.[3] The spectrophotometric method gave $k_2 = 1.2 \times 10^8$ M^{-1} s^{-1}.[4] From this agreement we can conclude that the relaxation observed spectrophotometrically doubtlessly corresponds to the dimeric association.

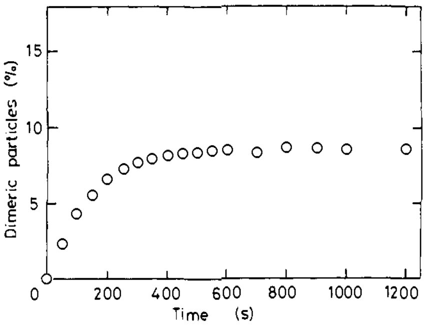

Figure 1. Time dependence of the percents of dimeric particles in the suspension at 25 °C ([MATA-2] = 8.1×10^{-11} M, [G-5301] = 8.1×10^{-12} M).

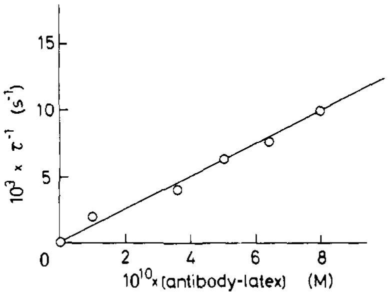

Figure 2. Influence of the concentration of the antibody–latex on the reciprocal of the relaxation time of the association of antibody–latex with antigen–latex at 25 °C.

Further, we examined an association of latex particles modified with human serum albumin (HSA) or anti-HSA-immunoglobulin G from rabbit (anti-HSA-IgG). Anti-HSA-IgG was purified by precipitation from 40% saturated ammonium sulfate, ion-exchange chromatography using a DEAE-Cellulose column, and immunological chromatography using a HSA-Sepharose column.[5,6] As a carrier of these proteins we used poly(acrolein-*co*-styrene) latex (AL-2, diameter 3750 Å, acrolein content in the latex 19%) modified with 6-aminohexanoic acid. Schiff base formed between the latex and the spacer molecule is reduced by a borane–dimethylamine complex.[7] HSA and anti-HSA-IgG were separately immobilized onto this latex particle by using a water-soluble carbodiimide, viz., 1-ethyl-3-(3-(dimethylamino)propyl)carbodiimide hydrochloride at pH 5. The number of proteins immobilized on the latex particle was about 16 000 for both antigen–latex and antibody–latex. The association process was studied at pH 8.7, where ζ-potentials of the latex particles were almost zero.

By mixing the suspension of antigen–latex with an excess amount of the antibody–latex suspension, we could observe the dimeric association of latex particles. Figure 2 shows the plot of the reciprocal of the relaxation times vs. concentration of antibody–latex. From the slope of the figure we could determine the second-order rate constant of interlatex association as 1.3×10^7 M^{-1} s^{-1}. This k_2 value is larger than that found by us for free HSA and anti-HSA-IgG (1.9×10^6 M^{-1} s^{-1})[8] because the local concentration of the reactants is much higher for the latex-bound case than for the free systems.

The present analysis is essentially two-dimensional, but it will be valid in the three-dimensional case, provided that the particle

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(1) 1 M denotes 6.02×10^{23} particles in 1 L of suspension.

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0002-7863/87/1509-1867$01.50/0

distribution is uniform in the suspension. We are presently examining a number of association processes using various colloidal particles.

Acknowledgment. We are grateful to Professor G. Hall for his useful comments and H.K. thanks Associate Professor T. Okubo for his discussion.

Presumably Planar Derivatives of Tribenzo[*a*,*c*,*e*]cyclooctene: Synthesis of 10,11-Methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene-1,14-dione and 1,1,14,14-Tetramethyl-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene[1]

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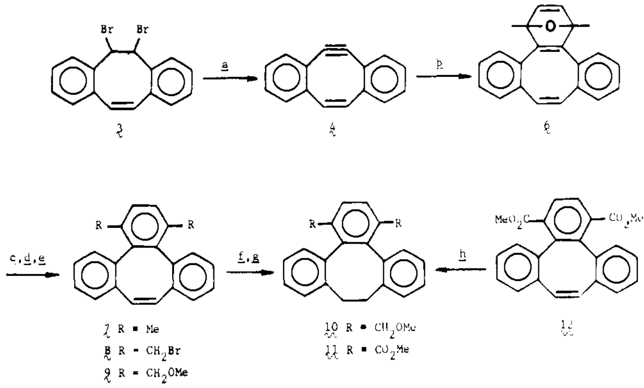
Received October 6, 1986

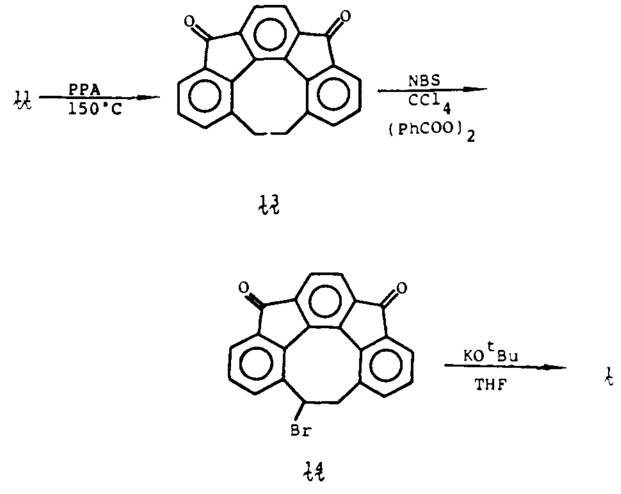
The intriguing properties exhibited by planar cyclooctatetraenes embedded in polycyclic frameworks have recently attracted considerable attention. Consequently, presumably coplanar derivatives of dibenzo[*a*,*c*]cyclooctene fused with carbocycles or heterocycles, i.e., cycloocta[*def*]biphenylene,[3] cycloocta[*def*]fluorene,[4] and cycloocta[*def*]carbazole,[5] as well as tetraphenylene derivatives fused with cyclopentanoids[6] and furans[7] have been synthesized. Their properties have also been studied. On the other hand, no attention has been given to the synthesis of coplanar derivatives of tribenzo[*a*,*c*,*e*]cyclooctene. The reason of this might be attributed to the fact that substituted tribenzo[*a*,*c*,*e*]cyclooctenes are not readily available.

Scheme I[a]

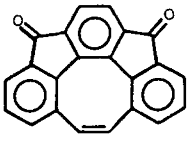


[a](a) KO-*t*-Bu,THF; (b) 2,5-dimethylfuran; (c) $TiCl_4$, $LiAlH_4$, Et_3N, THF; (d) NBS, CCl_4; (e) NaOMe, MeOH; (f) H_2, 10% Pd–C, EtOAc; (g) $RuO_2{\cdot}H_2O$, $NaIO_4$, CCl_4, CH_3CN, H_2O; (h) H_2, 10% Pd–C, EtOAc.

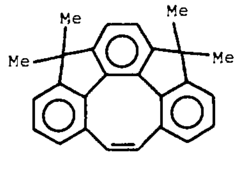
Scheme II



As part of a program aimed at the synthesis of novel coplanar derivatives of tribenzo[*a*,*c*,*e*]cyclooctene, we have recently prepared 1,4-disubstituted tribenzo[*a*,*c*,*e*]cyclooctenes.[8] Encouraged by these results, we set forth to apply appropriate Friedel–Crafts cyclization to these 1,4-disubstituted tribenzo[*a*,*c*,*e*]cyclooctenes in the hope of synthesizing hitherto unknown coplanar derivatives of tribenzo[*a*,*c*,*e*]cyclooctene. We report here the successful synthesis of 10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-*def*]fluorene-1,14-dione (**1**) and 1,1,14,14-tetramethyl-10,11-methano-1*H*-benzo[5,6]cycloocta[1,2,3,4-def]fluorene (**2**).



1



2

Dehydrobromination of dibromide **3** with KO-*t*-Bu in THF yielded alkyne **4**[9] which was allowed to undergo Diels–Alder cycloaddition with 2,5-dimethylfuran (**5**).[8] The adduct 1,4-endoxide **6** was isolated in 63% yield.[8] Deoxygenation of **6** with low-valent titanium[10] furnished 1,4-dimethyltribenzo[*a*,*c*,*e*]cyclooctene (**7**).[8] Treatment of **7** with excess NBS provided 55% of dibromide **8**[8] together with 14% of a monobromide.[8] The dibromide **8** was then converted to methyl ether **9** in 67% yield by reaction with sodium methoxide in methanol. The methyl ether **9** formed colorless crystals:[11] mp 138–139 °C; ^{1}H NMR ($CDCl_3$) δ 3.05 (s, 6 H), 3.93, 4.20 (dd, AB, J = 12 Hz, 4 H), 6.60 (s,

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