The Reaction of Solid Phenylmethanes with Potassium

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Solid phenylmethanes and potassium were purified by repeated high-vacuum distillation and their reaction was studied at 10^{-7} torr. The reaction between diphenylmethane and potassium occurs with liberation of hydrogen, benzene, and toluene. Triphenylmethane and potassium yield hydrogen and benzene whereas the reaction of tetraphenylmethane with potassium yields a negative ion which is stable in solid state and in solution. The ultraviolet spectra of the compounds dissolved in tetrahydrofuran and in 1,4-dioxane were measured. The compounds probably are ion-pair complexes which dissociate in the relatively polar tetrahydrofuran to a greater extent than in 1,4-dioxane. From the temperature dependence of the molar conductance, the enthalpies of dissociation were determined and found to be positive when the compounds were dissolved in 1,4-dioxane and negative when tetrahydrofuran was used as solvent.

Theilacker and Mölhoff[2] reported that sodium metal reacts with dissolved triphenylmethane, without liberation of hydrogen, to form a mixture of diphenylmethylsodium and triphenylmethylsodium. The corresponding reaction with solid triphenylmethane, however, occurs with liberation of hydrogen.[3] In the present paper we wish to give further information on the reaction of solid phenylmethanes with potassium.

Mass spectrometric analyses of the formed gaseous products indicated that the reaction between potassium metal and solid triphenylmethane occurs with liberation of hydrogen and benzene. This result can be explained by the reaction mechanism shown in Scheme I.

Triphenylmethane (I) is reduced by acceptance of one electron from the potassium metal. The formed negative ion (II) is not of planar structure; therefore resonance of the additional electron with the π electrons of the three benzene rings should be weak. Cleavage of one hydrogen atom or one phenyl radical (reactions 2 and 3) would yield planar and therefore more stable compounds: triphenylmethylpotassium (III) and diphenylmethylpotassium (IV). Benzene and hydrogen are then formed through secondary reactions (reactions 4 and 5). The existence of the primarily formed negative ion (II) could be proved indirectly: the decomposition of the solid reaction compounds with carbon dioxide occurred with liberation of hydrogen owing to reaction 6.

The composition of the released gases remained constant after 2 weeks, indicating that the reaction had stopped. The hydrogen pressure was 6×10^{-3} torr, the benzene pressure was 23×10^{-3} torr, and the pressure of the hydrogen liberated through the reaction of the undecomposed negative ion (II) with carbon dioxide was 6×10^{-3} torr. Evaluation of these data on the basis of the described reaction mechanism indicates that, after the reaction had stopped, approximately 50% of the negative ions of triphenylmethane had been decomposed according to reaction 2, 33% according to reaction 3, and 17% remained undecomposed.

Mass spectrometric analyses of the gases liberated through the reaction of diphenylmethane with potassium indicate hydrogen, benzene, and toluene. The result can be interpreted by means of a reaction mechanism (Scheme II) quite similar to the one mentioned above.

Again the hydrocarbon is reduced by the potassium, and cleavage of the negative ion (II) occurs. Cleavage of one hydrogen atom or one phenyl radical would yield diphenylmethylpotassium (III) and benzylpotassium (IV), respectively. The latter subsequently reacts with diphenylmethane according to the known reaction (4), with formation of toluene and again diphenylmethylpotassium (III). Hydrogen and benzene are then formed through secondary reactions 5 and 6. The decomposition of the solid potassium compounds with carbon dioxide again releases hydrogen, much less, though, than in the case of the corresponding ion of triphenylmethane.

An equilibrium pressure had not been observed after 10 weeks. At that time the hydrogen pressure was 1.00 torr, the benzene pressure was 0.17 torr, and the pressure of the hydrogen released by the decomposition of the negative ion (II) with carbon dioxide, according to reaction 7, was determined as being 0.8×10^{-2} torr. The data indicated that about 92% of the primarily formed negative ions of diphenylmethane had been decomposed according to reaction 2, about 7% according to reaction 3, and that less than 1% was still undecomposed

The reaction of tetraphenylmethane with potassium yields a negative ion which is stable in solid state as well as in solution. The initial hydrocarbon could be completely recovered by shaking the solution of the potassium compound in 1,4-dioxane with mercury, and was identified through its ultraviolet spectrum. Apparently resonance of the additional electron with the π electrons of the four benzene rings of the negative ion of tetraphenylmethane is sufficient for its stability, in spite of the nonplanar structure of the compound.

The investigated potassium compounds are colored, and the ultraviolet spectra of the solutions in 1,4-dioxane and in tetrahydrofuran show absorption bands in the visible range. The yellow solution of diphenylmethylpotassium, formed by reaction of diphenylmethane with potassium, has its main absorption maximum at 23.0×10^3 cm^{-1} (Figure 1). The reaction of triphenylmethane with potassium yields a mixture of diphenylmethylpotassium and triphenylmethylpotassium, according to the above-mentioned reaction

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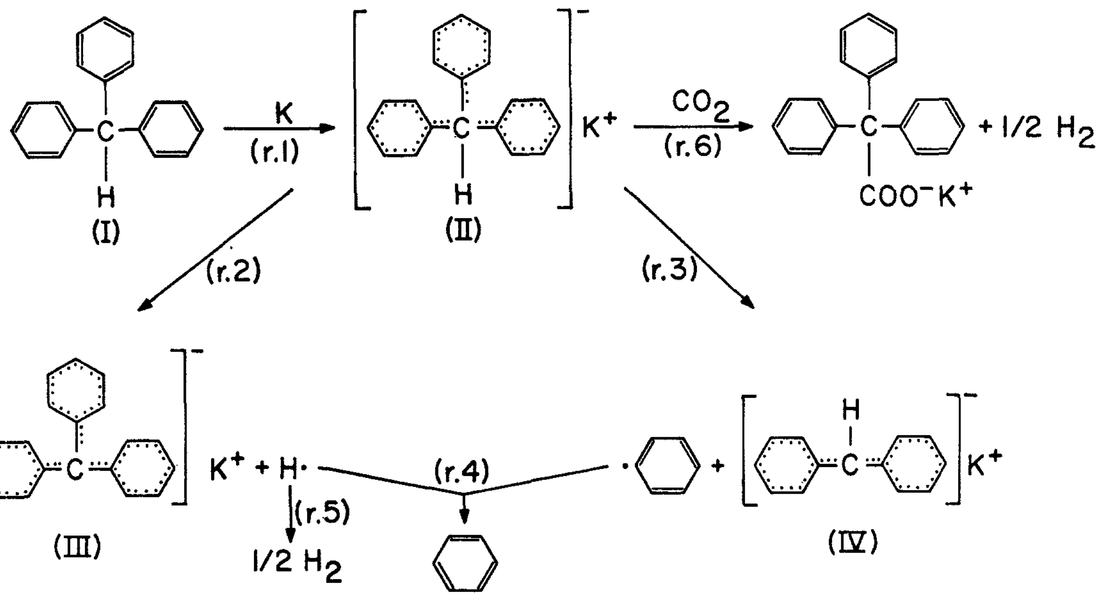
[1] (a) Adapted from a portion of the Ph.D. thesis of K. K. Brandes conducted at the Technische Hochschule Hannover, Hannover, Germany. (b) To whom inquiries should be directed at the Georgia Institute of Technology.

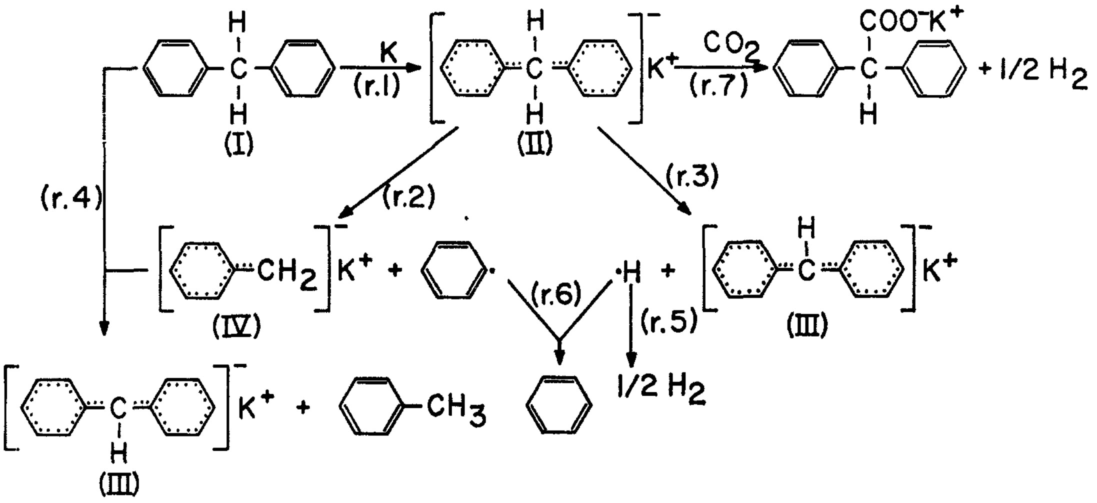
[2] W. Theilacker and E. Mölhoff, *Angew. Chem.*, **20**, 781 (1962).

[3] H. F. Meyer, Ph.D. Thesis, Technische Hochschule Hannover, Hannover, Germany, 1960.

SCHEME I



SCHEME II



mechanism. Therefore the orange solution of the reaction compounds in 1,4-dioxane has two absorption bands (Figure 2): at 23.0 × 10^3 cm^{-1} owing to diphenylmethylpotassium, and at 20.9 × 10^3 cm^{-1} in accordance with data obtained for triphenylmethylsodium.[4] The red solution of the potassium compound of tetraphenylmethane in 1,4-dioxane shows a wide absorption band at 20.5 × 10^3 cm^{-1} (Figure 3).

The molar conductances of the solutions of the potassium compounds, dissolved in 1,4-dioxane at room temperature, are in the range of 10^{-9} to 10^{-8} ohm^{-1} × cm^2 × $mole^{-1}$ and increase with temperature (Figure 4). The molar electric conductances of the corresponding solutions in tetrahydrofuran (Figure 5) pass through maxima and are in the range of 10^{-3} to 10^{-2} ohm^{-1} × cm^2 × $mole^{-1}$. These results indicate a strong polar bond between the alkali metal and the hydrocarbon. Probably the potassium compounds formed through reaction of diphenyl-, triphenyl-, and tetraphenylmethane are ion pair complexes which dissociate in the relatively polar tetrahydrofuran (dielectric constant 7.8) to a much greater extent than in 1,4-dioxane (dielectric constant 2.2).

The electric dissociation and the viscosity are the main influences in the temperature dependence of the electric conductance of a dissolved ionic compound. The Debye–Hückel interionic interaction is neglected for solutions as dilute as those used for the investigated compounds (1 to 4 × 10^{-4} mole/l.) and because for the small temperature ranges considered (in this case a 25° range) the electric conductance changes linearly with temperature. With

$$\Lambda_c = (\text{constant})\,\frac{1}{\eta}\,(c_{A^+} + c_{B^-}) = (\text{constant}')\,\frac{1}{\eta}\,c_{A^+} \quad (1)$$

where Λ_c is the molar conductance, η is the viscosity coefficient, and c_{A^+} and c_{B^-} are the concentrations of the ions formed from 1 mole of the compound AB and

$$k_d = \frac{c_{A^+}c_{B^-}}{c_{AB}} \quad (2)$$

where k_d is the dissociation constant, one obtains

$$\Lambda_c = (\text{constant}')\,\frac{1}{\eta}\,k_d \quad (3)$$

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(4) L. C. Andersen, *J. Am. Chem. Soc.*, **57**, 1673 (1935).

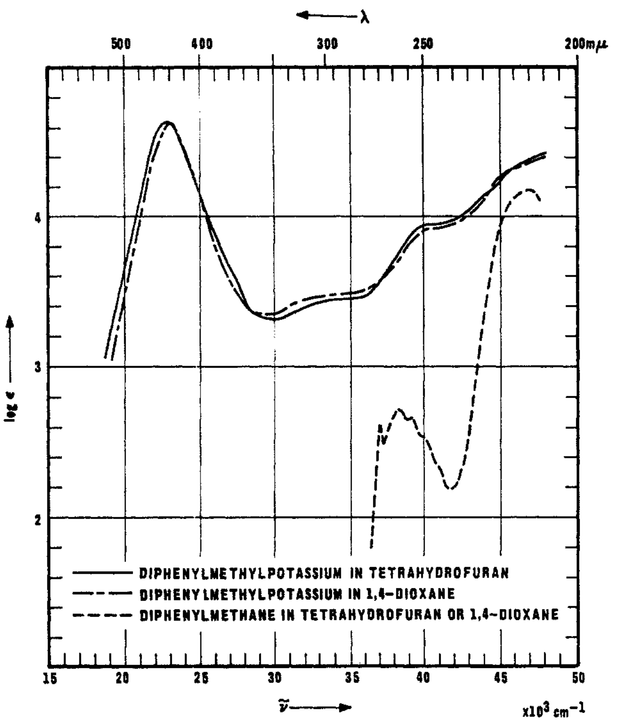

Figure 1.—Spectra of the solutions of diphenylmethylpotassium in tetrahydrofuran (c 1.8 × 10^{-4} mole/l.) and in 1,4-dioxane (c 2.3 × 10^{-4} mole/l.), and of diphenylmethane in tetrahydrofuran or 1,4-dioxane.

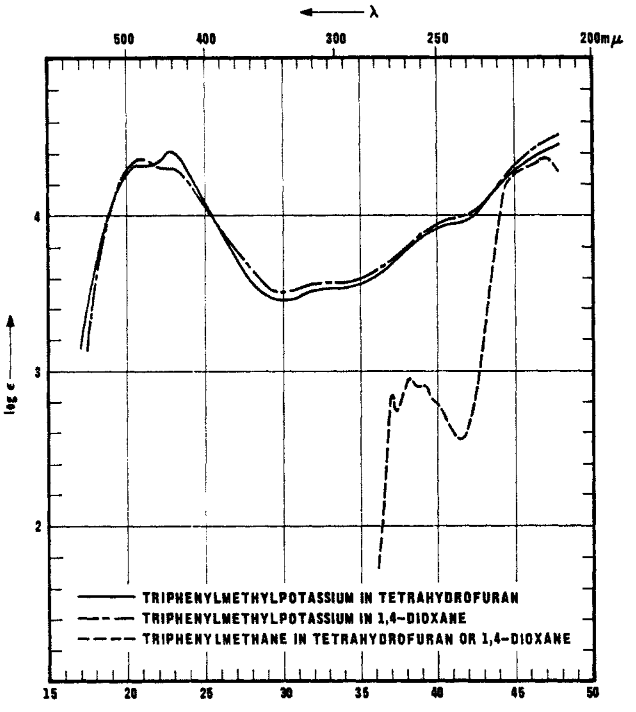

Figure 2.—Spectra of the solutions of triphenylmethylpotassium in tetrahydrofuran (c 1.9 × 10^{-4} mole/l.) and in 1,4-dioxane (c 1.4 × 10^{-4} mole/l.), and of triphenylmethane in tetrahydrofuran or 1,4-dioxane. As indicated in the reaction mechanism for triphenylmethane the solutions of triphenylmethylpotassium in 1,4-dioxane and in tetrahydrofuran contain about 5 × 10^{-5} mole/l. of diphenylmethylpotassium.

if k_d is small, $c_{A^+} = c_{B^-}$, and c_{AB} is unity. Writing eq 3 in logarithmic form and substituting for k_d from the van't Hoff law, $\ln k_d = -\Delta H_d/RT +$ (constant) will lead to the expression

$$\log \Lambda_c + \log \eta = (\text{constant}'') - \frac{\log e}{2R} \Delta H_d \times \frac{1}{T} \quad (4)$$

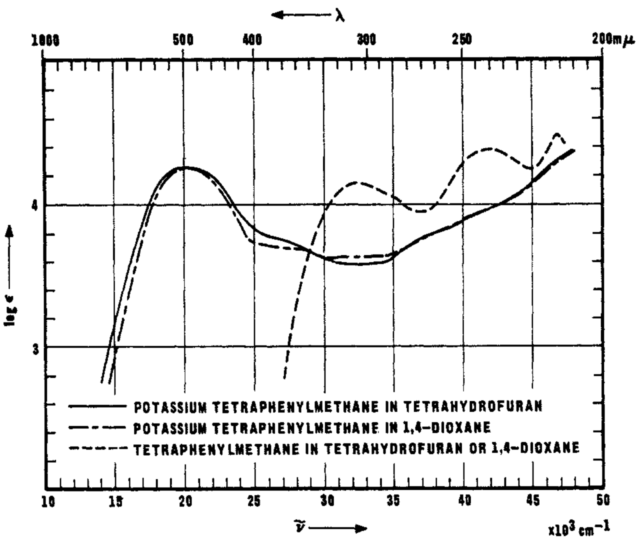

Figure 3.—Spectra of the solutions of potassium tetraphenylmethane in tetrahydrofuran (c 2.2 × 10^{-4} mole/l.) and in 1,4-dioxane (c 3.7 × 10^{-4} mole/l.), and of tetraphenylmethane in tetrahydrofuran or 1,4-dioxane.

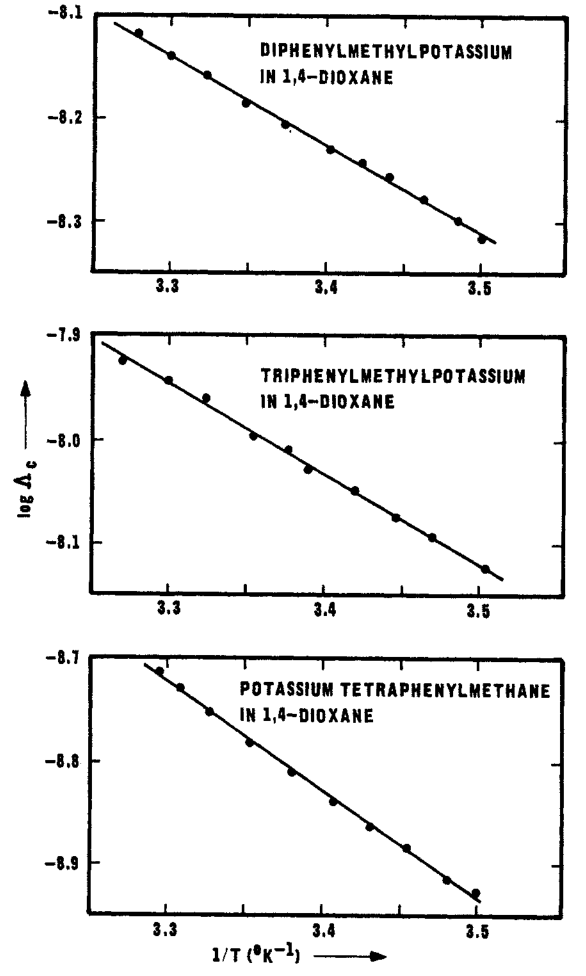

Figure 4.—Logarithm of the molar conductance as a function of $1/T$ of diphenylmethylpotassium (c 2.3 × 10^{-4} mole/l.), triphenylmethylpotassium (c 1.4 × 10^{-4} mole/l.), and potassium tetraphenylmethane (c 3.7 × 10^{-4} mole/l.) dissolved in 1,4-dioxane. The solution of triphenylmethylpotassium contains about 5 × 10^{-5} mole/l. of diphenylmethylpotassium.

Thus, the enthalpies of dissociation can be calculated from the gradients of the straight lines which are obtained by plotting log Λ_c and log η *vs.* $1/T$. In the case of 1,4-dioxane as solvent this yields straight

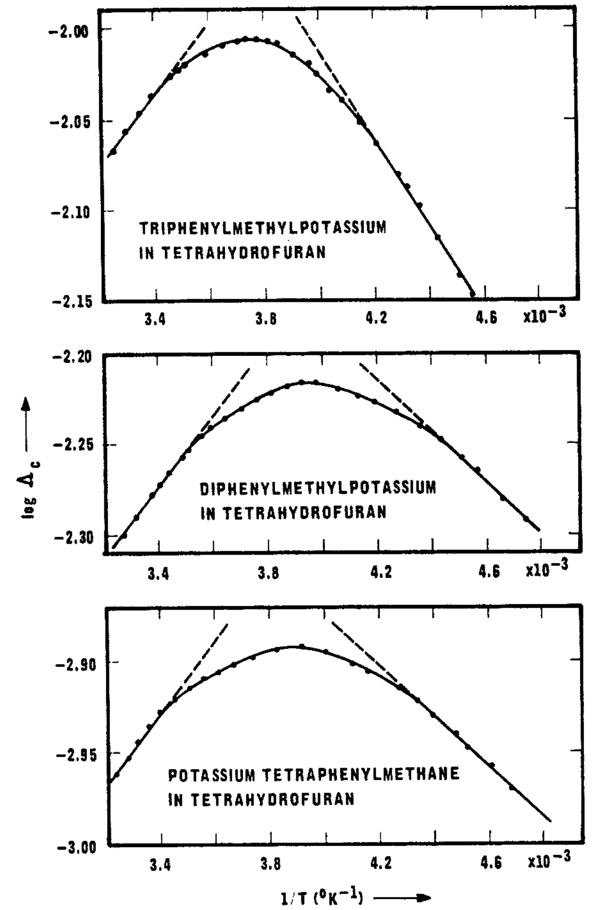

Figure 5.—Logarithm of the molar conductance as a function of $1/T$ of triphenylmethylpotassium (c 1.9 × 10^{-4} mole/l.), diphenylmethylpotassium (c 1.8 × 10^{-4} mole/l.), and potassium tetraphenylmethane (c 2.2 × 10^{-4} mole/l.) dissolved in tetrahydrofuran. The solution of triphenylmethylpotassium contains about 5 × 10^{-6} mole/l. of diphenylmethylpotassium.

lines (Figure 4). For tetrahydrofuran as solvent, maxima in the range of −18 to −9° are obtained. However, the ascending and descending branches can be approximated by straight lines (Figure 5). In Figure 6 log $\eta^{5,6}$ is plotted against $1/T$. The enthalpies of dissociation of the investigated compounds, as obtained from a plot of log Λ_c + log η *vs.* $1/T$, are listed in Table I.

The enthalpy of dissociation can be considered as composed of the positive ion-pair bonding energy and the negative enthalpy of solvation. Since the ion-pair bonding energies depend only on the nature of the ion-pair compound, the ΔH_d values of Table I signify that the enthalpy of solvation is approximately 8 kcal/mole more negative in the range of 10 to 35° if the dissociation occurs in tetrahydrofuran rather than in 1,4-dioxane. The enthalpies of solvation in tetrahydrofuran, furthermore, are less negative at lower temperatures. This result is in agreement with results obtained for the potassium compounds of naphthalene and anthracene dissolved in the same solvent.[7]

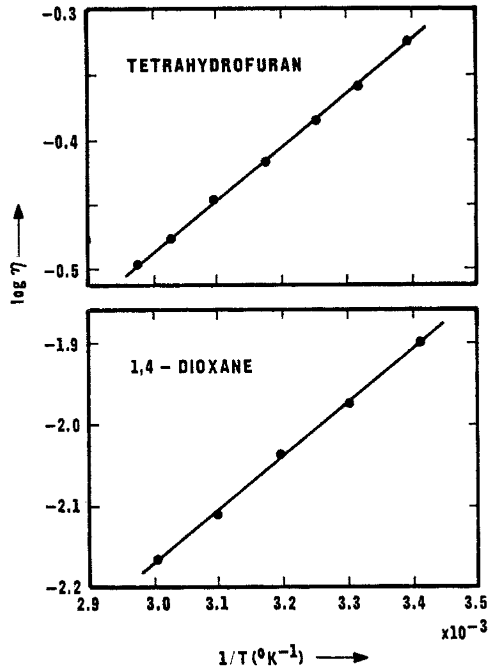

Figure 6.—Logarithm of the viscosity coefficient as a function of $1/T$ for tetrahydrofuran and 1,4-dioxane.

TABLE I

MOLAR ENTHALPIES OF DISSOCIATION

Compd	Solvent	Temp, °C	ΔH_d, kcal/mole
Diphenylmethylpotassium	1,4-Dioxane	10 to 35	+2.01
Mixture of di- and triphenylmethylpotassium	1,4-Dioxane	10 to 35	+2.10
Potassium tetraphenylmethane	1,4-Dioxane	10 to 35	+3.82
Diphenylmethylpotassium	Tetrahydrofuran	10 to 35	−5.58
Diphenylmethylpotassium	Tetrahydrofuran	−60 to −35	−2.41
Mixture of di- and triphenylmethylpotassium	Tetrahydrofuran	10 to 35	−5.38
Mixture of di- and triphenylmethylpotassium	Tetrahydrofuran	−60 to −35	−1.53
Potassium tetraphenylmethane	Tetrahydrofuran	10 to 35	−5.62
Potassium tetraphenylmethane	Tetrahydrofuran	−60 to −35	−2.51

Experimental Section

Reagents.—Potassium was prepared from $K_2Cr_2O_7$ and zirconium metal[8] and was degassed by repeated distillation in a high vacuum apparatus at 10^{-7} torr.

Diphenyl-, triphenyl-, and tetraphenylmethane were recrystallized several times from ethanol, and were dried and degassed through high-vacuum sublimation (10^{-7} torr).

Carbon dioxide was formed by heating magnesium carbonate at 380° in a high-vacuum apparatus. The gas was dried over a potassium film and was frozen out by cooling several sample tubes with liquid nitrogen. More volatile gases, such as hydrogen and oxygen, were pumped off.

1,4-Dioxane and tetrahydrofuran were purified according to the method by Pestemer,[9] and then rectified over sodium wire in a stream of dry nitrogen. The purified solvents were dried

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(5) W. Hertz and E. Lorentz, *Z. Physik. Chem.*, **A140**, 409 (1929).

(6) η for tetrahydrofuran: Professor Dr. Kuss, Technische Hochschule Hannover, Hannover, Germany, private communication, 1963; also C. Carvajal, K. J. Tolle, J. Smid, and M. Szwarc, *J. Am. Chem. Soc.*, **87**, 5548 (1965).

(7) K. K. Brandes and R. J. Gerdes, *J. Phys. Chem.*, **71**, 508 (1967).

(8) J. H. de Boer, J. Broos, and H. Emmens, *Z. Anorg. Allgem. Chem.*, **191**, 113 (1930).

(9) M. Pestemer, *Angew. Chem.*, **63**, 118 (1951); **67**, 740 (1955).

over a potassium film in a glass bulb which had been sealed off under high-vacuum conditions. They were degassed by alternate solidification and melting in a 10^{-7}-torr pressure. Finally all substances were collected in sample tubes equipped with break-seal valves and were then sealed off from the high-vacuum apparatus.

Procedures and Measurements.—Reactions of the solid phenylmethanes with potassium were carried out in a 1-l. glass bulb. A potassium film was formed by distilling the metal out of a sample tube into the bulb, under good high-vacuum conditions (10^{-7} torr). Subsequently the bulb was sealed off from the high-vacuum apparatus, and the hydrocarbon was sublimed onto the metal film. After the reaction had taken place the bulb was attached to a mass spectrometer (CH4, Atlas, Bremen) in order to analyze the volatile reaction compounds. The mass spectrometer was equipped with a capacitance manometre for partial pressure determination. The bulb was then evacuated to 10^{-5} torr and an attached sample tube containing carbon dioxide was opened. The additional release of any gaseous compounds was determined mass spectrometrically.

Solutions of the solid potassium compounds were prepared in a glass apparatus which consisted of a sample tube with the solvent, a glass bulb with the solid potassium compound, and several optical and conductivity cells. The apparatus was sealed off after it had been baked out at 400° for about 10 hr in a 10^{-7} torr vacuum. The break-seal valves above the sample tube and the bulb were opened and a small amount of the solid potassium compound was dissolved. The solution (about 50 ml) was then poured through a sealed-in glass frit into measurement cells which were subsequently sealed off.

The concentration of the solutions was determined by potentiometric titration of the potassium hydroxide, formed by hydrolizing the solutions. The ultraviolet spectra were measured by means of a spectrophotometer (H 700 308, Hilger and Watts, London). A picoamperemeter (Knick, Berlin) was used for determining low electric conductivity data of solutions in 1,4-dioxane. Higher conductivity data of solutions in tetrahydrofuran were measured by means of a Wheatstone bridge.

Registry No.—Diphenylmethylpotassium, 10060-17-0; diphenylmethane, 101-81-5; triphenylmethylpotassium, 1528-27-4; triphenylmethane, 517-16-8; potassium tetraphenylmethane, 10036-54-1; tetraphenylmethane, 630-76-2.

Perchloric Acid Catalyzed Aromatic Mercuration in Acetic Acid Solution. I. Electrophilic Reagents[1,2]

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The rate of the perchloric acid catalyzed mercuration of benzene by mercuric acetate or mercuric perchlorate in acetic acid solution at 25° is directly proportional to benzene concentration but is a complicated function of the concentration of the mercurating agent. The reaction is catalyzed strongly by perchloric acid, retarded weakly by water, and affected by sodium perchlorate in a way which depends on the acidity and water content of the reaction medium. These observations can be understood in terms of an acid-base reaction between perchloric acid and mercuric acetate which forms appreciable quantities of acetatomercury(II) perchlorate ion pairs; these, in turn, are protonated further to give small amounts of mercuric perchlorate ion triplets. Since water is weakly basic in acetic acid solution, it supresses these equilibria; sodium perchlorate affects the activity of water and also produces a small amount of perchloric acid through solvolysis. All three mercury-containing species, $Hg(OAc)_2$, $HgOAc^+ClO_4^-$, and $Hg^{2+}(ClO_4^-)_2$, are active mercurating agents which account for sizable portions of the mercuration reaction under different conditions; the relative reactivities of the first two toward benzene at 25° stand in the ratio $1:10^4$.

Aromatic mercuration in acetic acid solution has been of considerable value in providing data to test proposed quantitative treatments of aromatic substitution: rates and isomer distributions for mercuration by mercuric acetate are now available for benzene and toluene,[5] the monoalkylbenzenes and polymethylbenzenes,[6] anisole,[7] biphenyl and fluorene,[8] and the halobenzenes.[9] Unfortunately, it is difficult to extend these studies to aromatic substrates containing appreciably deactivating substituents, for here the reaction of mercuric acetate with aromatic substrate is very slow and, at the high temperatures which must be used, mercuric acetate is not stable in acetic acid solution.[5,9]

Perchloric acid is known to accelerate the rate of aromatic mercuration in acetic acid solution very strongly.[5,10] This catalyzed reaction would therefore seem to provide a good system in which to obtain rate and isomer distribution data for aromatic substrates with deactivating substituents. In contrast to the situation for aromatic mercuration in aqueous solution,[11] however, comparatively little research seems to have been done on the kinetics and mechanism of perchloric acid catalyzed mercuration in acetic acid solution, and there appear, moreover, to be points of disagreement even in the little information which is available. Before attempting to provide quantitative data for deactivated aromatics, we therefore decided to undertake a detailed mechanistic study of aromatic mercuration in acetic acid solution with special emphasis on catalysis by perchloric acid.

We soon discovered that the perchloric acid catalyzed reaction is relatively complex: it involves the

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(1) Directive Effects in Aromatic Substitution. LIX.

(2) Based in part upon a thesis submitted by M. Dubeck to Purdue University in partial fulfillment of requirements for the degree of Doctor of Philosophy.

(3) Postdoctoral Research Associate at Purdue University, 1954–1955, on projects supported by grants from the National Science Foundation (No. G-2752) and the Atomic Energy Commission [No. At(11-1)-170].

(4) Monsanto Chemical Co. Fellow at Purdue University, 1956–1957.

(5) H. C. Brown and C. W. McGary, Jr., *J. Am. Chem. Soc.*, **77**, 2306 (1955).

(6) H. C. Brown and C. W. McGary, Jr., *ibid.*, **77**, 2310 (1955).

(7) H. C. Brown and M. Dubeck, *ibid.*, **82**, 1939 (1960).

(8) H. C. Brown, M. Dubeck, and G. Goldman, *ibid.*, **84**, 1229 (1962).

(9) H. C. Brown and G. Goldman, *ibid.*, **84**, 1650 (1962).

(10) R. M. Schramm, W. J. Klapproth, and F. H. Westheimer, *J. Phys. Colloid Chem.*, **55**, 843 (1951).

(11) C. Perrin and F. H. Westheimer, *J. Am. Chem. Soc.*, **85**, 2733 (1963).