

ently, the substitution reaction also occurs during the synthesis, but concomitantly with oxidation of the catalyst and deposition of elemental carbon. At synthesis temperatures (210–250°), the replacement of nitrogen by carbon proceeded somewhat more rapidly at 21.4 atmospheres than at 7.8 atmospheres, but in every case considerably more slowly than observed by Jack at 450°. The nitrogen content of the catalyst was never decreased below atom ratios of N/Fe of 0.14, nor was Hägg carbide observed in the used nitrated catalysts. Although all the nitrated catalysts were quite resistant to oxidation and deposition of elemental carbon at 7.8 atmospheres, these reactions proceeded much faster in some catalysts at 21.4 atmospheres. However, the stability and activity of nitrated catalysts were much greater at both pressures than those of reduced catalyst. The stability of fused catalysts at 21.4 atmospheres varied considerably with the type of structural promoter. Thus, the catalysts promoted with alumina or zirconia were much more resistant to oxidation than the magnesia-promoted catalyst.

The rate of removal of nitrogen from the catalyst was relatively independent of the composition of the

synthesis gas, indicating that the hydrogenation of nitrides was strongly inhibited by carbon monoxide and/or synthesis products. In pure hydrogen, iron nitrides can be completely hydrogenated in a few minutes at synthesis temperatures.

When  $\epsilon$ -carbonitrides were reduced in hydrogen, most of the nitrogen was removed; however, the carbon content changed very little, and a part of the carbon appeared as carbide. That cementite was formed in X337 and Hägg carbide in X273 may be attributed to the differences in the temperatures of hydrogenation; however, the differences in catalyst type and composition, especially the presence or absence of copper, may be important in determining the nature of the carbide phase. In subsequent synthesis, the hydrogenated, used catalysts behaved like reduced catalysts in regard to their selectivity and tendency to oxidize.

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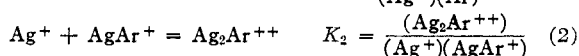
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, DAVIS CAMPUS OF THE UNIVERSITY OF CALIFORNIA]

## The Solubility of Toluene in Silver Perchlorate Solutions and the Absorption Spectra of the Toluene–Silver Complexes<sup>1</sup>

BY R. M. KEEFER AND L. J. ANDREWS

The solubilities of toluene in aqueous silver perchlorate–sodium perchlorate solutions of ionic strengths 1 and 5, as influenced by changes in silver ion concentration, have been determined. The ultraviolet absorption spectra of certain of these toluene–silver ion solutions also have been investigated. The results of these studies indicate that 1:1 and probably 2:1 silver ion–toluene complexes are present in these solutions.

The solubilities of a number of benzene derivatives in aqueous solutions containing varying amounts of silver nitrate (and sufficient potassium nitrate to adjust the ionic strength of the solvent to unity) have been measured.<sup>2</sup> The resultant data have been interpreted on the supposition that equilibria (1) and (2) were established in the saturated solutions.



To evaluate  $K_1$  and  $K_2$  an additional constant  $K$  has been defined as

$$K = \frac{(\text{Ar}_c)}{(\text{Ag}^+)(\text{Ar})} = K_1 + K_1K_2(\text{Ag}^+) \quad (3)$$

where

$(\text{Ar}_c)$  = molar concentration of complexed hydrocarbon =  $\frac{(\text{Ar}_c) - (\text{Ar})}{(\text{Ar}_c) - (\text{Ar})}$   
 $(\text{Ar}_c)$  = molar concentration of all hydrocarbon containing species

$(\text{Ar})$  = molar concentration of uncomplexed hydrocarbon = molar concentration of hydrocarbon in its saturated solution in 1 *N* potassium nitrate

$(\text{Ag}^+)$  = concentration of free silver ion in solution

The only evidence that  $\text{Ag}_2\text{Ar}^{++}$  actually was formed in these reactions was the fact that  $K$  values increased in a linear fashion with increasing silver ion concentration of the solvent, as required by eq. 3.

In the interpretation of the experimental data by the above equations the following assumptions were made regarding the properties of the aromatic substances and of the ions in solutions of different silver ion concentrations (but of fixed ionic strength): (1) The activity of the uncomplexed aromatic substance is the same in all solutions. This was arbitrarily chosen to equal the concentration of aromatic substance in 1 *M* potassium nitrate. (2) The activity coefficients of the two singly charged ions,  $\text{AgAr}^+$  and  $\text{Ag}^+$ , are equal. Thus the calculated values of  $K_1$  based on concentrations would closely approximate the thermodynamic equilibrium constant for eq. 1. The thermodynamic equilibrium constant for eq. 2 would be given by  $K_2(\gamma_{\text{Ag}_2\text{Ar}^{++}}/\gamma_{\text{Ag}^+}\gamma_{\text{AgAr}^+})$ . The activity coefficient term was assumed to be constant as long

(1) Paper number VIII in the series "Cation Complexes of Compounds Containing Carbon–Carbon Double Bonds."

(2) L. J. Andrews and R. M. Keefer, *THIS JOURNAL*, **71**, 3644 (1949); **72**, 3118 (1950); **72**, 5034 (1950).

as the ionic strength was unaltered. (3) The concentration of uncomplexed aromatic substance is the same in solutions of the same ionic strength.

Since the amount of water dissolved in the aromatic phase is very small the activity of the aromatic phase should be very close to that of the pure aromatic substance and essentially independent of the ionic constituents in the aqueous phase. Therefore the first assumption seems justified.

The second assumption seems reasonable since the ionic strength and the negative ion concentrations are the same for all solutions and since the silver and potassium ions, which are present in varying concentrations, are of similar size.

Of these assumptions the third is the least readily justified. Although it is doubtful that the concentration of uncomplexed aromatic substance in the saturated solutions is influenced sufficiently by the substitution of silver ions for potassium ions to account for the observed increase in  $K$  values, it has seemed important to attempt to clarify this point.<sup>3</sup>

Therefore further argentation studies on toluene, a compound typical of those investigated previously, have been made. These studies include a series of measurements of the solubility of toluene in aqueous silver perchlorate-sodium perchlorate solutions [(Ag<sup>+</sup>) = 0.2-1.0  $N$ ] of ionic strengths 1 and 5. In addition the absorption spectra of several silver perchlorate solutions saturated with toluene were measured. The results of these experiments, as interpreted in this report, indicate that the 2:1 complex probably is formed.

### Experimental

**The Solubility Measurements.**—G. Frederick Smith Chemical Co. anhydrous silver perchlorate and sodium perchlorate monohydrate were used to prepare solutions for the solubility measurements. The silver perchlorate solutions were standardized after preparation, and concentrations were assigned to the sodium perchlorate solutions on the basis of weight of the solid salt as removed from a freshly opened bottle. These solutions were mixed in appropriate amount to provide two series of solutions of ionic strengths approximating 1 and 5, in which the silver ion concentrations varied from about 0.2 to 1  $N$ . These solutions were saturated with toluene at 25° as described previously.<sup>2</sup> The saturated solutions were analyzed for total toluene concentration by extracting measured volumes with known volumes of hexane and determining the toluene concentration of the hexane phase spectrophotometrically by measuring its optical density at 260  $m\mu$  ( $\epsilon_{260\ m\mu}$  for toluene is 183).<sup>2</sup>

**The Absorption Spectra of the Complexes.**—Several silver perchlorate solutions in which the silver ion concentrations varied from 0.981-0.0491  $M$  (and in which the ionic strength was maintained at 1 by the addition of sodium perchlorate) were saturated with toluene at 25°. Samples of these solutions were measured at 25° on the Beckman spectrophotometer using 1-cm. cells over a wave length range of about 290-240  $m\mu$  (provided, as needed, with 9 mm. spacers to obtain readings in wave length regions of high intensity absorption). In most cases the blank cell contained a saturated solution of toluene in 1  $M$  sodium perchlorate.

Additional measurements on the spectrum of silver perchlorate and of toluene in water were also made.

All extinction coefficients,  $\epsilon$ , reported in this paper are calculated from the optical densities,  $d$ , using the expression  $d = \log_{10} I_0/I = \epsilon lc$  where  $c$  is the molar concentration of the

(3) The uncertainty as to the concentration of uncomplexed aromatic substance in the silver ion solution is reflected in the values of  $K$  as calculated by eq. 3 because of the resulting uncertainties in the values of the numerator of this equation.

absorbing substance and  $l$  is the path length in cm. of the absorption cell.

### Results

Table I gives the experimentally determined solubilities of toluene in aqueous silver perchlorate solutions (at  $\mu$  1.0 and  $\mu$  5.0) and in aqueous silver

TABLE I

THE SOLUBILITY OF TOLUENE IN AQUEOUS SOLUTIONS CONTAINING SILVER ION AT 25.0°

AgClO <sub>4</sub> , mole/liter	$\mu = 1.0$		AgNO <sub>3</sub> , mole/liter	$\mu = 1.0$	
	$T_s$ , mole/liter $\times 10^3$	$K$		$T_s$ , mole/liter $\times 10^3$	$K$
0	5.05		0	5.05	
0.185	7.66	2.84	0.200	7.80	2.76
.370	10.8	3.13	.400	10.73	2.86
.555	14.1	3.28	.600	13.88	2.96
.740	17.8	3.47	.800	17.48	3.12
.925	21.4	3.56	1.00	21.0	3.21
1.00	23.8	3.78			
$K_1 = 2.63$		$K_2 = 0.44$	$K_1 = 2.63$		$K_2 = 0.23$
$\mu = 5.0$					
0	1.26				
0.199	2.78	6.1			
.398	4.55	6.6			
.596	6.36	6.8			
.795	8.53	7.3			
.994	10.62	7.5			
$K_1 = 5.8$		$K_2 = 0.32$			

nitrate solutions (at  $\mu$  1.0). Silver perchlorate-sodium perchlorate solutions were used because the high solubility of sodium perchlorate allowed measurements at high ionic strengths. It also seemed of interest to compare the silver perchlorate and silver nitrate data to determine whether the negative ion had any specific influence on the toluene-silver complexes.

The solubility of toluene in the aqueous silver nitrate solutions as reported here is about 10% higher than reported previously<sup>2</sup> and is in good agreement with the several values reported by other investigators.<sup>4</sup> It is apparent from Table I that the calculated values of  $K$  (eq. 3) increase with increasing silver ion concentration both at ionic strengths of 1 and 5.<sup>5</sup> Plots of  $K$  versus silver ion concentration give straight lines. The values of  $K_1$  and  $K_2$  obtained from such plots are recorded in Table I. The measured solubilities might be explained solely in terms of the formation of a 1:1 complex ion (eq. 1) if it is assumed that silver ion can exert a strong salting in effect for toluene in aqueous solution (exclusive of that resulting from complex formation).

In general electrolytes exert a salting out effect on neutral molecules.<sup>6</sup> To test the generality of this statement as applied to toluene its solubility in various electrolyte solutions was measured (Table II). With the exception of perchloric acid all of the electrolytes which were tested caused

(4) R. L. Bohon and W. F. Claussen, *THIS JOURNAL*, **73**, 1571 (1951).

(5) In the calculations of  $K$  for the perchlorate solutions the term (Ar) has been taken as the molar concentration of toluene in its saturated solution in sodium perchlorate solutions of  $\mu$  1 or  $\mu$  5, as the case may be.

(6) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold Publishing Corp., New York, N. Y., 1943, p. 397.

TABLE II  
SOLUBILITY OF TOLUENE IN AQUEOUS SOLUTIONS AT 25°

Saturating solution	Toluene <sup>a</sup> concn., moles/liter × 10 <sup>3</sup>	$\frac{\log S_0/S}{\mu} = k_m^b$
Water	6.56	
1 M NaNO <sub>3</sub>	4.71	0.144
1 M KNO <sub>3</sub>	5.05	.114
1 M NaClO <sub>4</sub>	5.05	.114
1 M NaCl	3.96	.22
1 M KCl	4.14	.20
1 M HCl	5.81	.053
1 M HClO <sub>4</sub>	7.01	-.028
1 M NaOOC-CH <sub>3</sub>	4.06	.209

<sup>a</sup> Determined by the hexane extraction procedure.

<sup>b</sup> These values of the salting coefficients<sup>b</sup> are similar to those obtained in systems involving different neutral molecules.

a salting out effect, and the salting in effect of perchloric acid was slight. To obtain estimates of the salting effect of silver nitrate and silver perchlorate on neutral molecules the solubility of carbon tetrachloride at 25° was determined and found to be  $5.63 \times 10^{-3} M$  in water,  $4.74 \times 10^{-3} M$  in 1 M potassium nitrate,  $5.63 \times 10^{-3} M$  in 1 M silver nitrate and  $5.36 \times 10^{-3} M$  in 1 M silver perchlorate. Thus for carbon tetrachloride (similar results were obtained with chloroform) silver nitrate has no salting effect and silver perchlorate only a slight salting out effect. These salting effects may in-

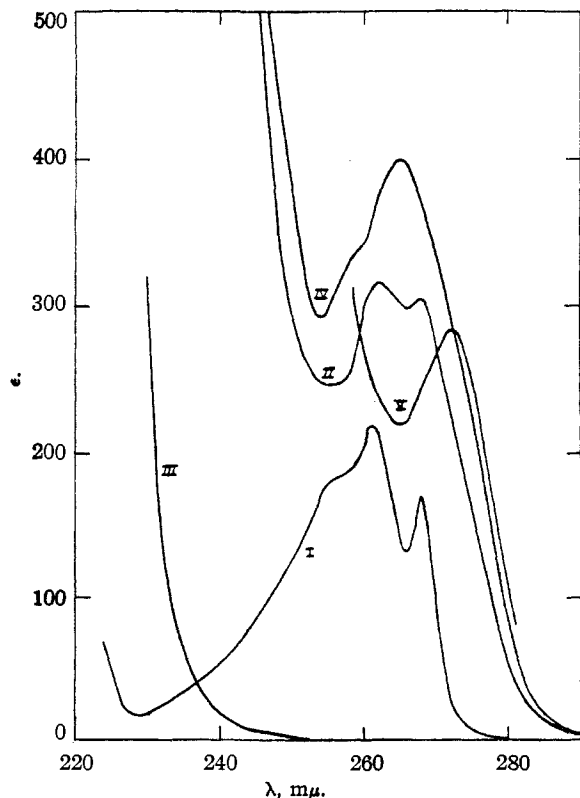


Fig. 1.—The absorption spectra of aqueous solutions of toluene, silver perchlorate and their complex ions: I, toluene in water; II, toluene saturated solution of 0.925 M AgClO<sub>4</sub> (0.925 M AgClO<sub>4</sub> in blank cell); III, 0.925 M AgClO<sub>4</sub>; IV, the AgT<sup>+</sup> complex in water; V, the Ag<sub>2</sub>T<sup>++</sup> complex in water.

clude small amounts of complex formation due to weak organic chloride-silver ion interactions.<sup>7</sup> Thus it appears to be improbable that silver nitrate would exert a strong salting in effect on toluene (exclusive of complex formation), and therefore that the doubly argentated complex ion may exist in solutions of high silver ion concentration.

This argument favoring the existence of the 2:1 complex is greatly strengthened by the fact that *K* values for solutions of ionic strength 5 (where the salting out or in effects due to exchanging part of the sodium ion by silver ion should be very small) again increase with increasing silver ion concentration of the medium.

Since *K*<sub>1</sub> is the same (at μ 1) for silver perchlorate and silver nitrate solutions, the nature of the negative ion can have no specific effect on the tendency for formation of the 1:1 complex. However, the replacement of nitrate by perchlorate ion does affect the magnitude of *K*<sub>2</sub> probably through its influence on the activity coefficient of the doubly charged complex ion.

**The Absorption Spectra of the Complexes.**—In Fig. 1 the absorption spectrum of toluene in water (curve I) is compared with that of a saturated solution of toluene in 0.925 M silver perchlorate (curve II). It should be noted that the latter curve, which was obtained from measurements using 0.925 M aqueous silver perchlorate as a blank, excludes the absorption of free silver ion in the solution. The recorded extinction coefficients are based on the total toluene content of the solutions as measured by the hexane extraction method of analysis. The spectrum of 0.925 M aqueous silver perchlorate solution<sup>8</sup> (curve III) is included for comparative purposes.<sup>9</sup>

The marked increase in intensity of absorption of the toluene solutions produced by silver ion must be attributed to the presence in the solutions of silver ion-toluene complexes. If the assumption that both 1:1 and 2:1 complexes are present in the silver ion-toluene solutions is correct, the measured optical densities, *d*, of the solutions (using water as a blank) should be related to the concentrations and extinction coefficients of the absorbing substances as indicated in eq. 4.

$$d = (\text{Ag}^+) \epsilon_{\text{Ag}^+} + (\text{T}) \epsilon_{\text{T}} + (\text{AgT}^+) \epsilon_1 + (\text{Ag}_2\text{T}^{++}) \epsilon_2 \quad (4)$$

For any solution for which the free silver ion and toluene concentrations are known a corrected optical density *d*<sub>c</sub>, as defined by equation (5), may be calculated.

$$d_c = d - (\text{Ag}^+) \epsilon_{\text{Ag}^+} - (\text{T}) \epsilon_{\text{T}} \quad (5)$$

It then should follow from equations 1, 2, 4 and 5 that

$$d_c/(\text{Ag}^+) = K_1(\text{T}) \epsilon_1 + K_1 K_2 (\text{T})(\text{Ag}^+) \epsilon_2 \quad (6)$$

Then a plot of *d*<sub>c</sub>/(Ag<sup>+</sup>) values (at any given wave length) against (Ag<sup>+</sup>) for a series of toluene saturated solutions of varying silver ion concentrations

(7) L. J. Andrews and R. M. Keefer, THIS JOURNAL, 74, 458 (1952).

(8) Cf. F. Volbert, Z. physik. Chem., 149A, 382 (1930).

(9) The spectrum of toluene in 1 N sodium perchlorate solution (measured against a 1 N sodium perchlorate blank) is identical with that of toluene in water. Sodium perchlorate and perchloric acid solutions (1 N) show no absorption in the wave length region of these measurements.

should yield a straight line of ordinate intercept  $K_1(T)\epsilon_1$  and of slope  $K_1K_2(T)\epsilon_2$ .

This procedure was applied to the spectrophotometric measurements of the toluene saturated silver perchlorate solutions of ionic strength unity, obtained as described in the experimental section, as a test for the existence of the 2:1 complex.<sup>10</sup> Representative plots of the data as analyzed by eq. 6 are given in Fig. 2. The values of  $d_c/(\text{Ag}^+)$  increase markedly with increasing silver ion concentration which may be taken as evidence that  $\text{Ag}_2\text{T}^{++}$  exists as a light absorbing substance in these solutions.

The values of  $\epsilon_1$  and  $\epsilon_2$  calculated from the data of these and similar plots for lower wave length measurements were used to plot the absorption spectra of  $\text{AgT}^+$  (curve IV) and  $\text{Ag}_2\text{T}^{++}$  (curve V) which appear in Fig. 1.

The accuracy of the interpretation of the data by eq. 6 is very limited below 260  $m\mu$ , because in this region the corrections to the measured optical densities for the absorption of free silver ion becomes appreciable as compared to the total absorption of the solutions. Also the optical densities in this region, except for those of solutions of low silver ion concentration, were in general too high to be measured accurately. Therefore the  $\text{Ag}_2\text{T}^{++}$  curve was not extended below 260  $m\mu$ , and the curve for  $\text{AgT}^+$  in this region must be regarded as only an approximation of the true curve.

It is interesting to note (curves 4 and 5) that when toluene becomes coordinated with silver ion, the toluene absorption in the near ultraviolet is somewhat enhanced. For the  $\text{AgT}^+$  complex the major alteration in the toluene spectrum occurs at lower wave length regions. The data available suggest that the 2:1 complex also begins to absorb strongly in the region of 250  $m\mu$ .

The evidence for the existence of  $\text{Ag}_2\text{T}^{++}$  as based on the absorption spectrum measurements is somewhat limited owing to the fact that the spectra of the complexes can be investigated conveniently in the ultraviolet only in a narrow wave length region in which toluene also shows appreciable absorption.

(10) In most of the measurements on these solutions the blank cell contained a toluene saturated solution of 1 *N* sodium perchlorate. Thus in these cases in correcting  $d$  values to obtain  $d_c$  it was assumed that the correction for the absorption of free toluene was not required. This assumption is particularly good in the wave length region from about 272–280  $m\mu$ , in which the toluene absorption is very small compared to that of the complex ions.

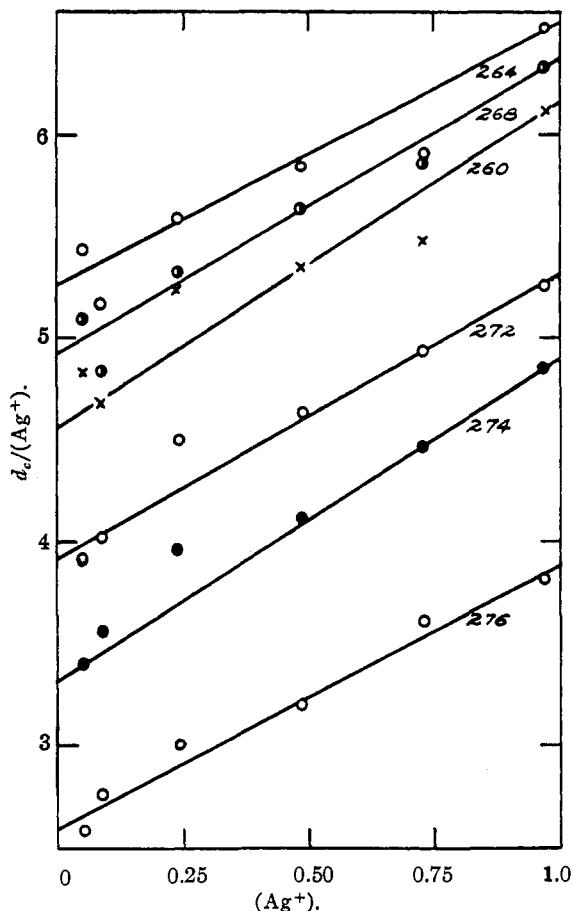


Fig. 2.—The optical densities of toluene saturated silver perchlorate solutions. The figures given just below and at the right of each line represent the wave lengths in  $m\mu$  for each series of measurements.

However, the combination of the spectral evidence and the evidence from the solubility studies seems to offer reasonably good proof that the  $K_2$  values, as obtained in this and previous work, may be considered as representative of 2:1 complex formation.

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