# ORGANIC AND BIOLOGICAL CHEMISTRY

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## Silver Salt–Olefin Complexes. I. Silver Nitrate Butadiene

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Under suitable conditions of pressure and temperature, a solid results from the interaction of butadiene with 8 *M* $AgNO_3$ solution. A study of the decomposition pressure of the dry solid indicated the presence of two complexes: $AgNO_3/C_4H_6$ and $(2AgNO_3)/C_4H_6$. The stoichiometry of the solid and the solubility of butadiene in $AgNO_3$ solution are discussed in the light of this information. The heats of reaction for the two species, as calculated from equilibrium data, are 10.8 and 13.0 kcal./mole, respectively.

### Introduction

While the preparation of a number of crystalline silver nitrate olefin complexes has been reported in the literature,[1-9] no material of this sort has been prepared directly from hydrocarbons having less than five carbons. A solid silver nitrate/butadiene complex has now been prepared. The object of this paper is to describe its formation and properties.

### Experimental

**Chemicals.**—The materials used in this study were reagent grade silver nitrate (Baker & Adamson Products, Allied Chemical Corp.) and C.P. grade 1,3-butadiene (The Matheson Co.).

**Procedure.**—Solubility studies and equilibrium pressure measurements were conducted in a conventional manometric apparatus comprising a vacuum manifold, gas transfer lines and calibrated vessels.

The anhydrous complex salt was prepared by passing butadiene gas through aqueous 8 *M* $AgNO_3$ at 15° and atmospheric pressure. The resulting precipitate was isolated on a fritted glass funnel by pressure filtration with butadiene gas and dried by passing butadiene gas over the crystals for 30 to 60 minutes with occasional stirring. The light yellow product was stored at −35° in a container sealed from light to prevent photochemical darkening. Equilibrium pressure data were obtained from portions of this material in a conventional manometric apparatus.

Preparatory to making equilibrium pressure measurements, the sample was pumped at −32° for 30 minutes. The thermostat bath was then adjusted to the desired temperature and periodic pressure readings were made until an equilibrium pressure was achieved.

### Results and Discussion

**Solubility Study.**—The solubility of butadiene in aqueous 8 *M* $AgNO_3$ at 15° is shown in Fig. 1. Under these conditions, the solubility of butadiene increased markedly with pressure to 0.5 mole of butadiene/mole of Ag. At this point, the pressure of butadiene above the solution was 662 mm. and the solution possessed a yellow color characteristic of silver complexes of conjugated dienes.[10] Shortly after the equilibrium pressure was recorded, a light yellow crystalline phase precipitated and the pressure decreased to 474 mm. This decrease in pressure corresponded to a calculated increase in butadiene solubility from 0.50 to 0.52 mole of butadiene/mole of Ag.

In another experiment, the attempt was made to exceed this ratio by the application of greater butadiene pressure. Due to the limitations of the apparatus, however, it was not possible to exceed 900 mm. Because of extremely slow equilibration (stirring was hampered by the crystalline phase) it was not possible to reach values significantly greater by this method. A discussion of these data is deferred until the remainder of the experimental results are described.

**Dissociation Studies.**—Equilibrium pressure data, presented in Fig. 2,[11] were obtained in the course of two experiments made with separate samples of the crystalline complex. In the first, presence of a second complex species was inferred from discontinuities in the data above 10° (see dotted line, Fig. 2). Since these data were too few in number and lacked sufficient precision, a second sample of the crystalline material was allowed to reach equilibrium at 15°, pumped rapidly to zero pressure, and allowed to establish a new set of equilibria (plot B, Fig. 2).

**Stoichiometry.**—At the conclusion of the first series of pressure measurements, the mixture of complexes was totally decomposed by heating, and a total of 0.100 mole of butadiene (analytically pure by mass spectrum) collected.[12] The residue contained 62.5% Ag (equivalent to 0.0153 mole of Ag) as compared to a theoretical 63.5% Ag in $AgNO_3$. Thus, the mole ratio of butadiene to silver was 0.65 for the dried mixture. A mole ratio of butadiene to silver greater than 0.5 and less than 1.0 is consistent with the reasonable inference that the material under study is a mixture of two complex silver salts, $AgNO_3/C_4H_6(s)$ and $(2AgNO_3)/C_4H_6(s)$.

The mole ratio of butadiene to silver for a mixture consisting of one part $(2AgNO_3)/C_4H_6(s)$ and one part $AgNO_3/C_4H_6(s)$ is 0.67. The amount of butadiene released by the decomposing species in the initial experiment up to the point where dissociation of a second species was inferred, was 0.00247 mole. This represents 25% of the total

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(11) Reversibility of complex formation under anhydrous conditions was demonstrated by raising and lowering the temperature and then allowing the system to return to equilibrium at a given temperature.

(12) Due to the instability of the complex material, it was not possible to obtain a carbon–hydrogen analysis.

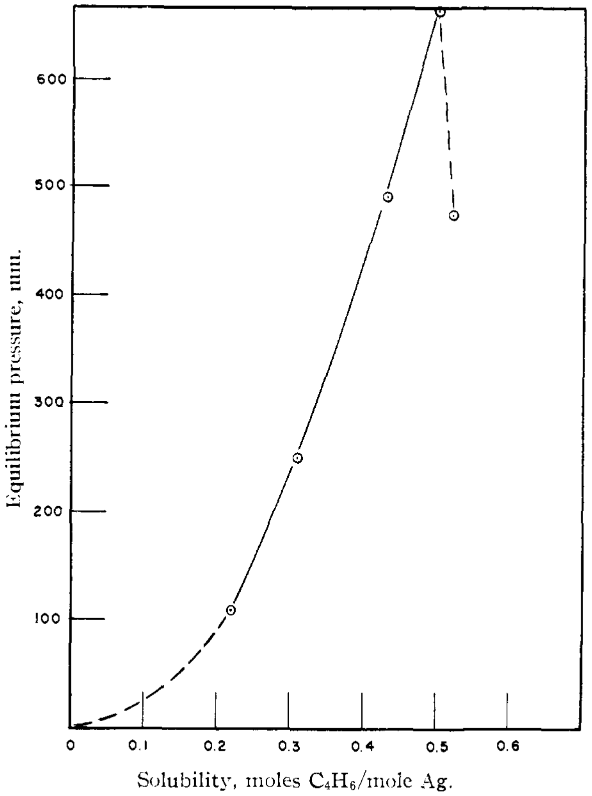

Fig. 1.—Butadiene solubility in 8 $M$ aqueous $AgNO_3$ at 15°.

butadiene complexes and is equivalent to the amount which would be released from $AgNO_3/C_4H_6(s)$ present in a 1-to-1 mixture (*cf.* eq. 1 and 2).[13]

$$2(AgNO_3/C_4H_6)(s) \rightleftarrows (2AgNO_3/C_4H_6(s) + C_4H_6(g) \quad (1)$$

$$(2AgNO_3)/C_4H_6(s) \rightleftarrows 2AgNO_3(s) + C_4H_6(g) \quad (2)$$

The analytical data thus appears to support a composition for the dried complex mixture which is 50% $AgNO_3/C_4H_6$ and 50% $(2AgNO_3)/C_4H_6$. Preparation of a material with greater butadiene content was attempted by the addition of gaseous butadiene to the dried complex salt at 20° (875 mm.) and at 25° (850 mm). Absorption of butadiene in these cases, however, appeared to be due to formation of polymer on the crystal surfaces and the attempt was discontinued.

We may now return to a discussion of the solubility data. The evidence obtained implies initial complex formation between two silver ions and one molecule of diolefin, that is, one silver ion per double bond. This reaction is described by the equilibrium

$$2AgNO_3(aq) + C_4H_6(g) \leftrightarrows (2AgNO_3)/C_4H_6(aq) \quad (3)$$

The shape of the solubility curve suggests that continued addition of butadiene results in supersaturation with respect to $(2AgNO_3)/C_4H_6(aq)$ until precipitation occurs. The increase in butadiene solubility accompanying precipitation points to the formation of the second complex species, $AgNO_3/C_4H_6$, by the equilibrium reaction

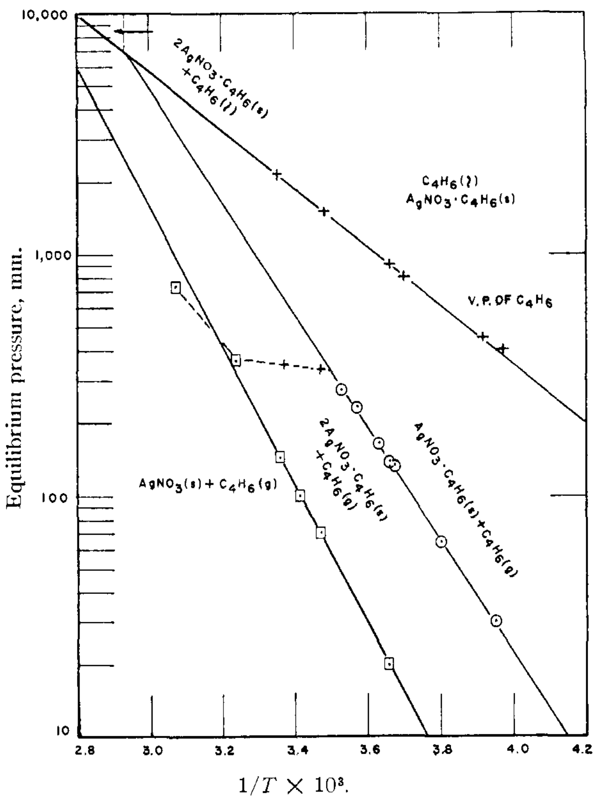

Fig. 2.—Decomposition pressures of silver butadiene complex salts: plot A (⊙), decomposition pressure of $AgNO_3/C_4H_6$; plot B (⊡), decomposition pressure of $(2AgNO_3)/C_4H_6$.

$$(2AgNO_3)/C_4H_6(aq) + C_4H_6(g) \rightleftarrows 2(AgNO_3/C_4H_6)(aq) \quad (4)$$

These phenomena are explained as follows: If the mole ratio of butadiene/silver in solution equals 0.50 and the pressure of butadiene above the solution is sufficient only to maintain this ratio, the sole species precipitating from the supersaturated solution would be $(2AgNO_3)/C_4H_6(s)$. However, when the pressure of butadiene above the solution is greater than this, there is a tendency for additional butadiene to be dissolved in accordance with the reaction in eq. 4. If the solubility of the species $AgNO_3/C_4H_6$ is sufficiently low, or if additional reaction takes place between solid $(2AgNO_3)/C_4H_6$ and $C_4H_6$ (*cf.* eq. 1), the precipitate will be a mixture of the two complexes. The apparent discrepancy between the mole ratio of butadiene to silver ion obtained from solubility studies (0.52) and that obtained from stoichiometric measurements of the crystalline phase (0.65) is explainable on the basis of the relatively large pressure of butadiene used during isolation. From a comparison between the decomposition pressure of $AgNO_3/C_4H_6(s)$ (Fig. 2) and the conditions prevailing during the isolation of the dried complex, it is readily seen that a pressure twice as great as the equilibrium pressure of butadiene necessary to

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[13] The equations represent a two-component, three-phase (and therefore) univariant system. The data presented in Fig. 2 are clearly compatible with this concept.

maintain the complex was present during isolation, forcing the reaction in eq. 1 to the left.

Thus, the mole ratio of butadiene to silver in the solid complex mixture is a function of the temperature and pressure prevailing during formation and isolation.

**Heats of Dissociation.**—Heats of dissociation, calculated from equilibrium data, are 10.8 and 13.0 kcal./mole, for $AgNO_3/C_4H_6(s)$ and $(2AgNO_3)/C_4H_6(s)$, respectively.

An extensive search of the literature failed to uncover any previous mention of a stable silver/butadiene complex salt, much less a mixture of two such salts, even though a number of silver/diene complex salts have been characterized.[1,4,14] However, the formation of a single complex salt, $(2CuCl)/C_4H_6(s)$, has been reported.[15,16]

Difference between the reported heat of dissociation of $(2CuCl)/C_4H_6(s)$ (17.0 kcal./mole) and that of $(2AgNO_3)/C_4H_6(s)$ (13.0 kcal./mole) can be attributed to the generally lower stability of a silver/olefin complex as compared to that of a copper/olefin complex.[17] A similar difference should exist between the heats of dissociation of the mono-metal-ion/diolefin salts. Unfortunately the formation of $CuCl/C_4H_6(s)$ has not been reported, although it is likely that, under suitable conditions, such a compound could exist. The heat of dissociation of $AgNO_3/C_4H_6$ (10.8 kcal./mole) is greater than that calculated for $AgNO_3$/1-butene (7.3 kcal./mole).[18] From this, it appears that the conjugated double bond supplies additional stabilization in complex formation. However, the nature of this stabilization is not evident from the present work.

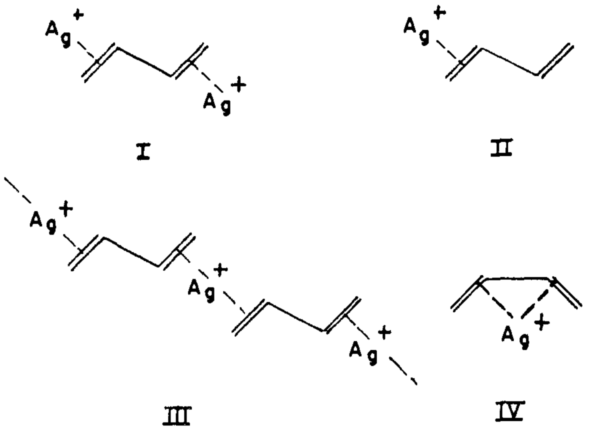

Fig. 3.

**Structure of the Complex Species.**—Since the butadiene molecule possesses two double bonds and it is generally accepted that these can act independently in complex formation,[19] a number of possibilities for the structures of the two complexes may be considered (Fig. 3). It may be assumed readily that the 2:1 complex has the structure I. In view of the discrepancy cited above between the heats of dissociation of the 1:1 complex and that of $AgNO_3$/1-butene, II would not appear to be a good possibility for the structure of solid 1:1. This objection may not, however, apply when this material is in solution. Structure III is similar to that proposed for a solid 1:1 $AgNO_3$/norbornadiene complex[14] and has the advantage that it would account for the ease with which interconvertibility between the 1:1 and the 2:1 complexes is accomplished in the solid phase. Such an interconversion is not readily visualized for structure IV which, however, in the absence of additional physical data, cannot be excluded and which does provide for the additional stabilization observed for the 1:1 complex.

**Acknowledgment.**—The authors wish to express their appreciation to Mr. R. Fischer for his able assistance with the experimental work and to Dr. E. Solomon for his valuable suggestions in preparing the manuscript.

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# Effect of Electric Charge on the Reactivity of Some Isoelectronic Free Radicals[1]

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Calculations are presented on the energetics of hydrogen atom abstraction reactions initiated by isoelectronic free radicals derived from oxygen or nitrogen compounds. Analysis of these results leads to the concept that positively charged species are inherently more reactive. Implications are discussed and acid catalysis of some free radical reactions is predicted under suitable conditions.

## Introduction

The extensive literature of free-radical chemistry is well reviewed in several recent publications[2-6] but it seems that only scant attention has been focused on an explicit comparison of the reactivity of a neutral free radical with its charged isoelectronic analogs. This neglect stems in large measure from the absence of comparative information on

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[1] The author is indebted to the Atomic Energy Commission for partial support of this contribution.

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