UCRL-17919
c.2

# University of California

# Ernest O. Lawrence Radiation Laboratory

## CHARGE TRANSFER COMPLEXES WITH HEXAFLUOROBENZENE AND PENTAFLUOROBENZONITRILE AS ACCEPTOR COMPONENTS

Gerald A. Corker and Melvin Calvin

October 31, 1967

TWO-WEEK LOAN COPY

*This is a Library Circulating Copy which may be borrowed for two weeks. For a personal retention copy, call Tech. Info. Division, Ext. 5545*

UCRL-17919 cy. 2

Submitted to Journal of Chemical Physics

UCRL-17919
Preprint

UNIVERSITY OF CALIFORNIA
Lawrence Radiation Laboratory
Berkeley, California

AEC Contract No. W-7405-eng-48

# CHARGE TRANSFER COMPLEXES WITH HEXAFLUOROBENZENE AND PENTAFLUOROBENZONITRILE AS ACCEPTOR COMPONENTS

Gerald A. Corker and Melvin Calvin

October 31, 1967

# Charge Transfer Complexes with Hexafluorobenzene and Pentafluorobenzonitrile as Acceptor Components*

GERALD A. CORKER‡ AND MELVIN CALVIN

Laboratory of Chemical Biodynamics and University of California

Berkeley, California

October 31, 1967

Charge transfer associations are a well-established phenomena and a rather extensively investigated one also.[1] Since the acceptor component of such complexes normally does not exist as a liquid under standard conditions,[2] we wish to report on two organic liquids which function as acceptor components with suitable complimentary molecules.

As indicated in Figure 1 (the presence of an extended shoulder in the spectra of the mixture), pentafluorobenzonitrile (PFBN) complexes with N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD), with N,N-dimethylaniline (DMA), and with phenothiazine in cyclohexane. In addition, crystalline complexes of TMPN-PFBN and DMA-PFBN are obtained when the pure materials are mixed.

These two organic bases also form solid complexes with hexafluorobenzene (HFB) when the materials are mixed in the pure state in a ratio of 1:1. However, new absorption bands are not detected in the spectra (in cyclohexane solutions) of mixtures of TMPD or DMA with HFB. When HFB is used as a solvent for TMPD or DMA, the solutions are visibly yellow. However, with time a reaction occurs as evident by the formation of a black precipitate.

The solid complex formed between TMPD-PFBN, which is orange, was analyzed by a combination extraction and spectroscopic method and by vapor phase chromatography and found to contain a ratio of the two components of 1:1 which agrees with an elemental analysis of this complex.

Analysis of DMA-PFBN or DMA-HFB complexes were complicated by the presence of excesses of the liquid components on the crystalline complexes. When attempts are made to dry the crystals, the crystals dissociate as the excesses evaporate until the crystals and the two components totally disappear. The TMPD-HFB complex was not analyzed. The complex between phenothiazine and PFBN was not isolated as a crystalline material.

The association constants for the TMPD-PFBN and DMA-PFBN complexes were determined according to the method of Hildebrand and Benesi.[3] The data obtained for these complexes, plotted according to the Hildebrand-Benesi equation, are shown in Figure 2. The association constants and extinction coefficients are given in Table I.

Although the NMR spectrum of the TMPD-PFBN complex suggested that free radicals were present in this complex (evidenced by line broadening compared to TMPD in $CCl_4$), no radical species could be detected by EPR in any of the complexes reported here; either in solution or in the solid complexes. Nor did illumination with ultraviolet or visible light produce a detectable level of paramagnetic species.

*This work was supported by the U.S. Atomic Energy Commission.

‡Present address: IBM Watson Laboratory, Columbia University, New York, N. Y.

1. F. J. Bullock, Comprehensive Biochemistry, M. Florkin and E. H. Stotz, Eds. (Elsevier Publishing Company, Amsterdam-London-New York, 1967).

2. G. Briegleb, Electron-Donator-Acceptor Komplexe, (Springer, Berlin, 1961).

3. H. Benesi and J. H. Hildebrand, J. Am. Chem. Soc. 70, 2832 (1948); 71, 2703 (1949).

TABLE I. Association constants and extinction coefficients for TMPD-PFBN and DMA-PFBN complexes

| Concentrations | | | K | | |
|---|---|---|---|---|---|
| PFBN | TMPD | DMA | (mμ) | (moles/l) | (l/mole cm) |
| 0.08 to 0.73 M | $5.0 \times 10^{-4}$ M | 0 | 380 | 4.0 | 800 |
| " " " | " " | 0 | 400 | 4.1 | 700 |
| " " " | " " | 0 | 420 | 4.3 | 600 |
| 0.07 to 0.66 M | 0 | $4.5 \times 10^{-3}$ M | 340 | 2.7 | 500 |
| " " " | 0 | " " | 350 | 3.1 | 400 |
| " " " | 0 | " " | 360 | 3.1 | 310 |

The cell path length was 1 cm in all these experiments.

## Figure Captions

Figure 1. Optical spectra in cyclohexane in one cm cells. (a) 1. 0.74 M PFBN, 2. $1.3 \times 10^{-3}$ M phenothiazine, 3. mixture of $1.3 \times 10^{-3}$ M phenothiazine and 0.11 M PFBN. (b) 1. 0.74 M PFBN, 2. $4.5 \times 10^{-3}$ M DMA, 3. mixture of $4.5 \times 10^{-3}$ M DMA and 0.66 M PFBN. (c) 1. 0.74 M PFBN, 2. $5.0 \times 10^{-4}$ M TMPD, 3. mixture of $5.0 \times 10^{-4}$ M TMPD and 0.74 M PFBN.

Figure 2. Hildebrand-Benesi plots of charge transfer absorption. (a) TMPD-PFBN complex at 380 mμ (closed triangles), 400 mμ (closed circles), and 420 mμ (crosses). (b) DMA-PFBN complex at 340 mμ (closed squares), 350 mμ (closed circles) and 360 mμ (crosses).

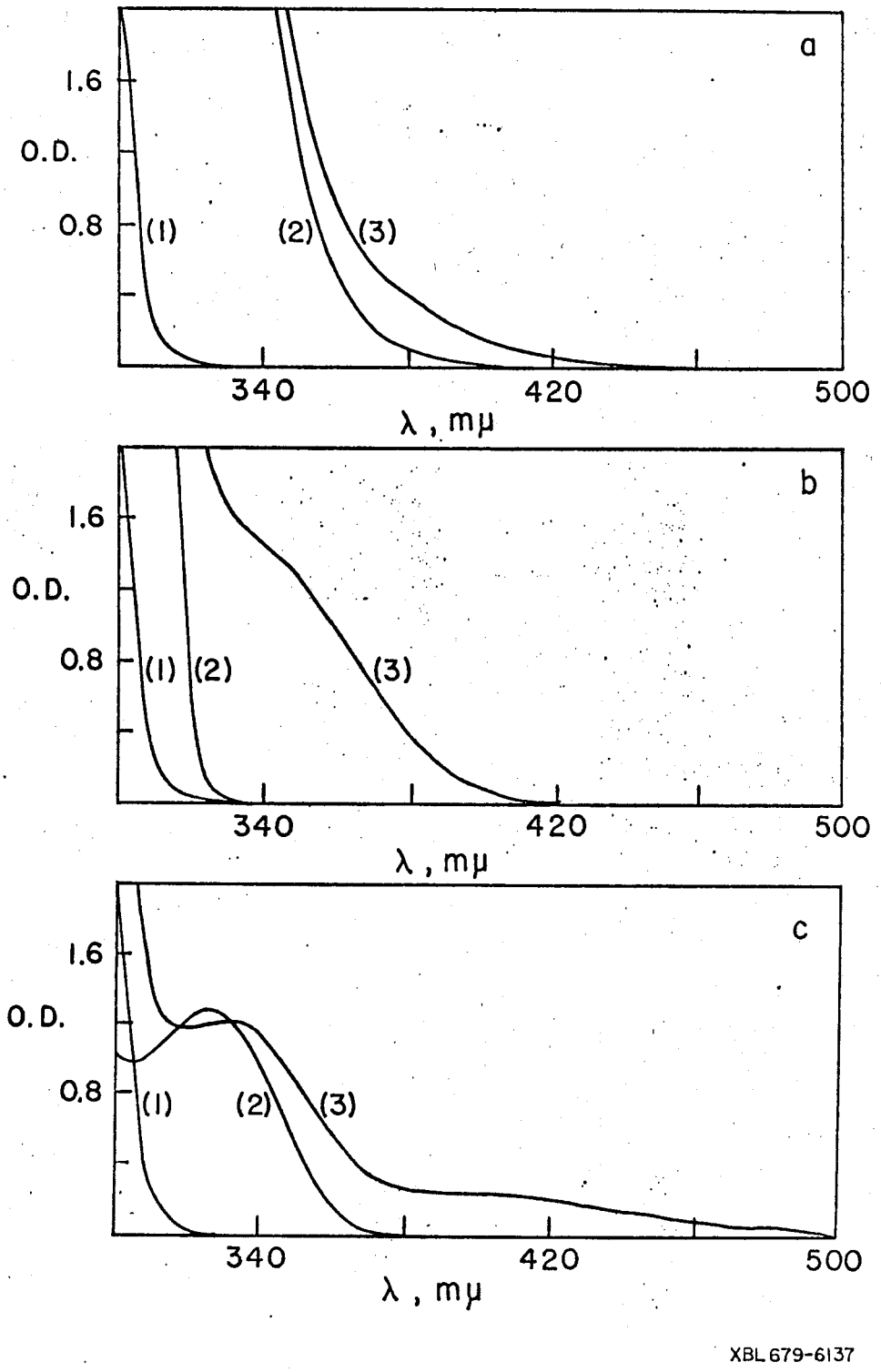
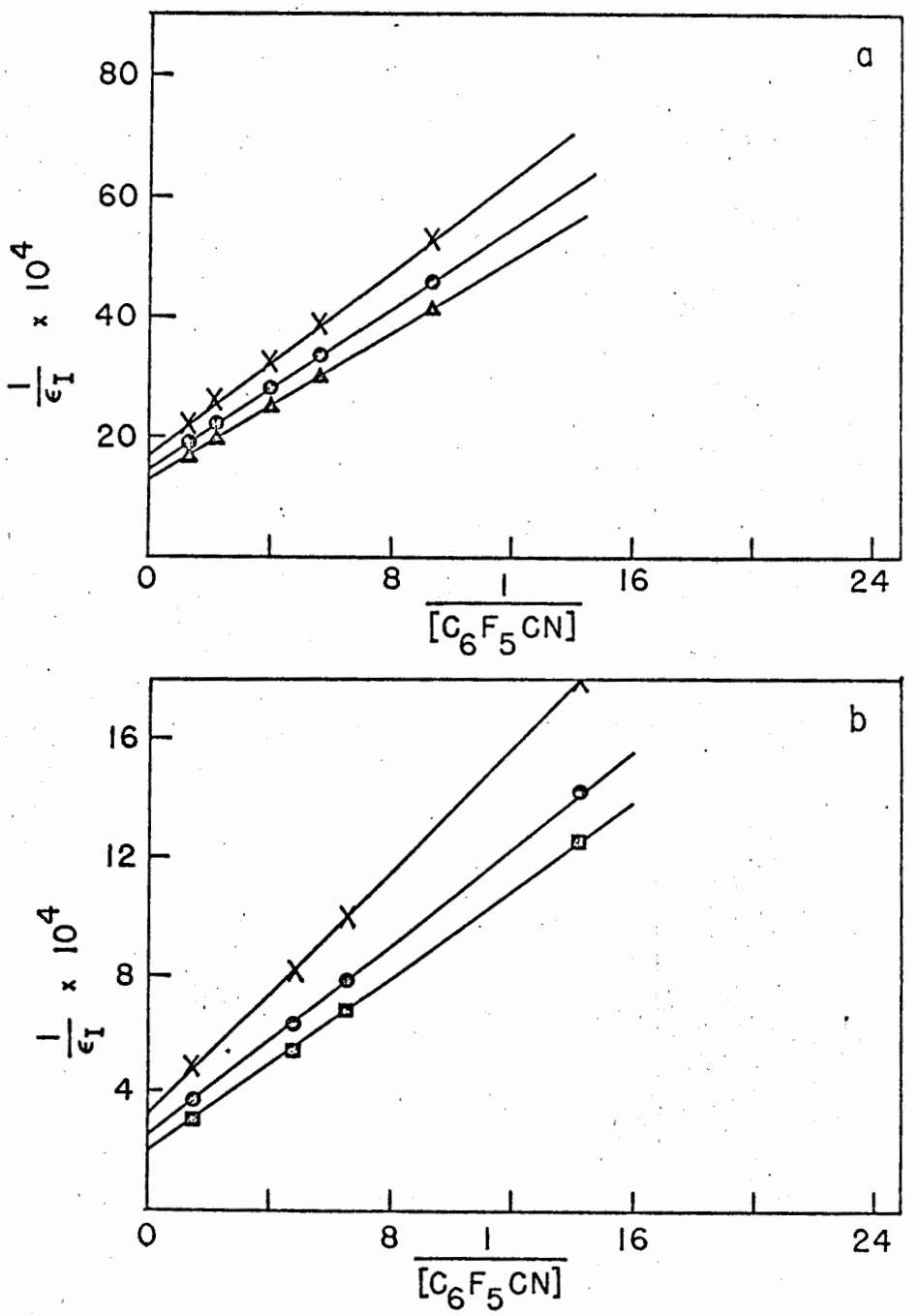

a
1.6
O.D.
0.8
(1)
(2)
(3)
340
420
500
λ , mμ
b
1.6
O.D.
0.8
(1)
(2)
(3)
340
420
500
λ , mμ
c
1.6
O.D.
0.8
(1)
(2)
(3)
340
420
500
λ , mμ
XBL 679-6137

Fig. 1




XBL 679-6134

Fig. 2

This report was prepared as an account of Government sponsored work. Neither the United States, nor the Commission, nor any person acting on behalf of the Commission:

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness, or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of any information, apparatus, method, or process disclosed in this report.

As used in the above, "person acting on behalf of the Commission" includes any employee or contractor of the Commission, or employee of such contractor, to the extent that such employee or contractor of the Commission, or employee of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Commission, or his employment with such contractor.