GEORGIA INSTITUTE OF TECHNOLOGY **OFFICE OF CONTRACT ADMINISTRATION**

PROJECT ADMINISTRATION DATA SHEET

☒ ORIGINAL ☐ REVISION NO. ______

Project No. G-33-661 (R6014-0A0) GTRC/~~GIT~~ XXX DATE 8 / 26 / 85

Project Director: Laren M. Tolbert School/~~Lab~~ XXX Chem

Sponsor: National Science Foundation

Type Agreement: Grant CHE-8513666

Award Period: From 8/1/85 To ~~1/31/87 *~~ 1/31/89 (Performance) ~~4/30/87~~ 4/31/88 (Reports)

Sponsor Amount: This Change / Total to Date

Estimated: $ ______ $ 199,000

Funded: $ ______ $ 73,000

Cost Sharing Amount: $ 738 Cost Sharing No: G-33-394

Title: Fundamentals of Carbanion Photochemistry (Chemistry)

ADMINISTRATIVE DATA OCA Contact John Schonk x4820

1) Sponsor Technical Contact:	2) Sponsor Admin/Contractual Matters:
~~Donald S. Slocum~~ Kenneth G. Hancock	~~Stephen C. Burnisky~~ Ommie H. Smith
National Science Foundation	National Science Foundation
MPS/CHE	DGC/MPS
Washington, DC 20550	Washington, DC 20550
202/357-7956	202/357-9671

Defense Priority Rating: N/A Military Security Classification: N/A

(or) Company/Industrial Proprietary: N/A

RESTRICTIONS

See Attached NSF Supplemental Information Sheet for Additional Requirements.

Travel: Foreign travel must have prior approval – Contact OCA in each case. Domestic travel requires sponsor approval where total will exceed greater of $500 or 125% of approved proposal budget category.

Equipment: Title vests with GIT

COMMENTS:

*Includes 6 month unfunded flexibility period.

No funds may be expended after 1/31/87.

AUG 1985
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Research Reports
Office

COPIES TO: SPONSOR'S I. D. NO. ______

Project Director
Research Administrative Network
Research Property Management
Accounting

Procurement/GTRI Supply Services
~~Research Security Services~~
Reports Coordinator (OCA)
Research Communications (2)

GTRC
Library
Project File
Other ______

12 / 88

GEORGIA INSTITUTE OF TECHNOLOGY
OFFICE OF CONTRACT ADMINISTRATION

NOTICE OF PROJECT CLOSEOUT

Date 7/27/89

roject No. G-33-661 **Center No.** R6014-0A0

roject Director L. M. Tolbert **School/Lab** Chem

ponsor NSF

ntract/Grant No. CHE-8513666 **GTRC** XX **GIT** ___

ime Contract No. ___

tle Fundamentals of Carbanion Photochemistry

fective Completion Date 1/31/89 (Performance) 4/30/89 (Reports)

oseout Actions Required:

- X None
- ___ Final Invoice or Copy of Last Invoice
- ___ Final Report of Inventions and/or Subcontracts
- ___ Government Property Inventory & Related Certificate
- ___ Classified Material Certificate
- ___ Release and Assignment
- ___ Other ___

cludes Subproject No(s). ___

bproject Under Main Project No. ___

ntinues Project No. ___ **Continued by Project No.** ___

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stribution:

- _ Project Director
- _ Administrative Network
- _ Accounting
- _ Procurement/GTRI Supply Services
- _ Research Property Management
- _ Research Security Services
- X Reports Coordinator (OCA)
- X GTRC
- X Project File
- X Contract Support Division (OCA)
- ___ Other ___

G-33-661

Del #2

Progress Report
NSF Grant CHE-8513666

Submitted by: **Laren M. Tolbert**
School of Chemistry
Georgia Institute of Technology
Atlanta, GA 30332

Progress.

The current NSF grant has supported the efforts of David Smith, a postdoctoral fellow from the University of Arkansas, Nurul Islam, a graduate student from the University of Kentucky, and Susan M. Fitzwater, a graduate student at Georgia Tech. Ms. Fitzwater has finished a project begun some time ago which examined substituent effects on carbanion photoexcited decay pathways. She has made the exciting discovery that, for carefully-controlled systems, such decay is controlled by an energy gap law effect. She is now turning her attention to proton transfer reactions in non-aqueous media, and has had some initial results which indicate that photoinitiated proton transfer using triethylamine is first order in base.

Dr. Smith finished the project involving electron-transfer to <u>cis</u>-1,2-diphenylcyclopropane. We have had to resolve some of our problems with intermediates by an appeal to time-resolved absorption spectroscopy, which the principal investigator has carried out at Argonne National Laboratories in collaboration with Dr. Michael Wasielewski. These studies are incomplete, but indicate that the electron carrier is both the solvent radical cation and solvated electron.

Mr. Islam has synthesized 1-phenylsulfinyl-2,6-diphenylcyclohexene. The conjugate base undergoes photodesulfinylation to yield an intermediate, not yet characterized, which we believe to be 1,3-diphenyl-1,2-cyclohexadiene, a strained allene. In the course of this work, he has developed a new synthesis of vinyl sulfides.

Finally, in an offshoot of this work, which focuses on the general question of proton transfer from transient acids, we have begun examining the kinetics of proton transfer from radical cations.

Expenditures and encumbrances as of 2-28-87 total $54,285. At the current rate, the remaining $5,981 in direct costs will be expended by May 31, 1987.

Active and Pending Grants.

(1) National Science Foundation, "Fundamentals of Carbanion Photochemistry," 8-1-85 to 1-31-89, $199,000.

(2) U. S. Department of Energy, "A Carbanion Approach to Polyacetylene," 7-1-85 to 6-31-88, $220,000 (projected).

(3) National Institutes of Health, "Biooxidation of Arylalkyl Hydrocarbons," 7-1-87 to 6-31-90, $268,361 direct costs (pending).

Publications (1986-).

L. M. Tolbert and R. K. Khanna, "A Dramatic Stereoelectronic Effect in a Biomimetic Oxidation: 9,10-Dialkylanthracenes," J. Am. Chem. Soc., in press.

A. Rajca and L. M. Tolbert, "How Does an Allene Distort to Accommodate Excess Negative Charge? 1,1,3,3-Tetraphenylallene." J. Am. Chem. Soc., in press.

A. Rajca, A. J. Streitwieser, Jr., and L. M. Tolbert, "Ab Initio Study of 2,3-Dilithiopropene," J. Am. Chem. Soc., in press.

L. M. Tolbert, "The Photoexcited States of Allyl Anions," Accts. Chem. Res. **19**, 268 (1986).

S. P. Webb, L. A. Phillips, S. W. Yeh, L. M. Tolbert, and J. H. Clark, "Picosecond Kinetics of the Excited-state, Proton-transfer Reaction of 1-Naphthol with Water," J. Phys. Chem. **90**, 5154 (1986).

L. M. Tolbert and J. A. Schomaker, "A Carbanion Approach to Doped Polyacetylene," Syn. Metals, **15**, 195 (1986).

L. M. Tolbert and J. A. Schomaker, "Polyanion Generation by Exhaustive Deprotonation of Poly(acetylene-co-1,3-butadiene)", Polym. Preprints (American Chemical Soc. Div. Polym. Chem.) **27**, 197 (1986).

C.P. Brock, J.C. Gregory, and L.M. Tolbert, "Structure of the cis,cis,cis,cis-1,2,3,4,5-Pentakis(methylsulfonyloxy)cyclopentane, Acta Cryst., C42, 1063 (1986).

G-33-661

TECH

School of Chemistry
(404) 894-4002

Georgia Institute of Technology
Atlanta, Georgia 30332
A Unit of the University System of Georgia

April 6, 1989

Dr. Seymour Lapporte
Organic Chemical Dynamics
Division of Chemistry
National Science Foundation
Washington, D. C. 20550

Dear Dr. Lapporte:

Subj: Form 98A for CHE-8513666.

I am enclosing a copy of my final report for my previous NSF grant, which formally expired January 1. You will receive the appropriate financial statement from our grants office. Please let me know if everything is in order. I checked the "previously furnished" box for the citations and list of collaborators, since this was included with my NSF renewal.

With best wishes,

Laren M. Tolbert,
Professor of Chemistry

CC: Office of Contract Administration

APPENDIX VII

NATIONAL SCIENCE FOUNDATION
Washington, D.C. 20550

FINAL PROJECT REPORT
NSF FORM 98A

PLEASE READ INSTRUCTIONS ON REVERSE BEFORE COMPLETING

PART I—PROJECT IDENTIFICATION INFORMATION

1. Institution and Address: Georgia Institute of Technol. Atlanta, GA 30332
2. NSF Program: Organic Dynamics
3. NSF Award Number: CHE-8513666
4. Award Period: From 7/1/85 To 1/31/89
5. Cumulative Award Amount: $199,000
6. Project Title: Fundamentals of Carbanion Photochemistry

PART II—SUMMARY OF COMPLETED PROJECT *(FOR PUBLIC USE)*

Carbanions are energy-rich species derived by deprotonation of carbon acids. Photoexcitation places such species at an even higher energy level which, without proper constraints, leads to electron expulsion. Certain resonance-stabilized carbanions, however, are bound with respect to photoejection, but exhibit a new charge distribution reflecting population of different molecular orbitals. This project has addressed fundamental aspects of carbanion photochemistry in the following ways: First, models for the carbanionic excited state based upon approximate molecular orbital theory have been developed. For example, 1-phenylallyl anions show enhanced charge density at carbon 2 in the excited state. Second, the photophysics of photoexcited carbanions have been compared with the predicted model. In the case of 9-phenylfluorenyl anion and related species, time-resolved emission and absorption spectroscopy have revealed that this non-alternant hydrocarbon anion is <u>not</u> characterized by an intramolecular charge transfer state, unlike the predicted model. Third, these studies have allowed rational design of precursors to a number of strained and reactive intermediates at ambient temperatures. For instance, substituted 2-chlorocyclohexenyl anions undergo halide expulsion to yield strained allenes, i. e., substituted 1,2-cyclohexadienes, the result of increased charge density at atom 2. In a related project which sought to use photoexcited carbanions as high potential electron donors, the reluctantly formed radical anion of 1,2-diphenylcyclopropane was produced by electron-transfer from photoexcited triphenylmethyl anion. Finally, these studies have been used to design new substrates for photoexcited proton transfer.

PART III—TECHNICAL INFORMATION *(FOR PROGRAM MANAGEMENT USES)*

1. ITEM *(Check appropriate blocks)*	NONE	ATTACHED	PREVIOUSLY FURNISHED	TO BE FURNISHED SEPARATELY TO PROGRAM	
				Check (✓)	Approx. Date
a. Abstracts of Theses	✓				
b. Publication Citations			✓		
c. Data on Scientific Collaborators			✓		
d. Information on Inventions	✓				
e. Technical Description of Project and Results	▨		✓		
f. Other *(specify)*	▨				

2. Principal Investigator/Project Director Name *(Typed)*: Laren M. Tolbert
3. Principal Investigator/Project Director Signature:
4. Date: 4/6/89

NSF Form 98A (3-83) Supersedes All Previous Editions

Form Approved OMB No. 3145-0058