

An Unusual Effect of Temperature on the Chromatographic Behavior of Buckminsterfullerene

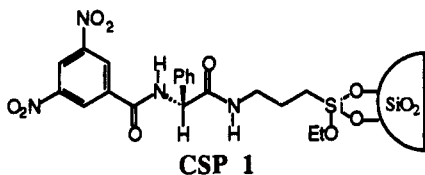
William H. Pirkle* and Christopher J. Welch

School of Chemical Sciences, University of Illinois, Urbana, Illinois 61801

Received September 9, 1991

Summary: An unusual increase in retention with increasing column temperature observed in the HPLC separation of buckminsterfullerene (C_{60}) and the related compound, C_{70} , on a π -acidic stationary phase has been exploited for improved preparative separations of these compounds at elevated temperatures.

Recent interest in the spherical carbon cluster, buckminsterfullerene (C_{60}), and the related compound, C_{70} , has stemmed from improved methods for the preparative synthesis of these intriguing compounds.^{1,2} Hawkins recently described³ the chromatographic separation of these compounds using a π -acidic chiral stationary phase (CSP 1),⁴ the chirality being incidental to the separation. The chromatographic purification of C_{60}/C_{70} using alumina¹ or a π -acidic dinitroaniline stationary phase⁵ has also been reported. While such purification is straightforward at the analytical level, large-scale purifications are rendered difficult owing to the insolubility of the C_{60}/C_{70} mixture. For example, C_{60} and C_{70} are but slightly soluble in benzene or toluene, two of the better solvents for this purpose. This severely limits the amount of material which can be successfully purified on a column containing CSP 1. Use of benzene or toluene as a mobile phase results in virtually no retention of C_{60} and C_{70} on CSP 1. Using a hexane mobile phase, retention is adequate so long as relatively small volumes of benzene (or toluene) solutions of C_{60}/C_{70} are injected onto the column. Injection of larger volumes causes very broad bands and poor resolution, as the injection solvent sweeps the C_{60}/C_{70} along the column. It is frequently noted that injection of analytes in a solvent other than the mobile phase leads to chromatographic abnormalities.⁶



In evaluating stationary phases, chromatographic separations are frequently conducted at various temperatures in order to determine the thermodynamic parameters of adsorption. Although the magnitudes of the enthalpy and entropy of adsorption vary considerably from analyte to analyte, the signs of both ΔH and ΔS are almost invariably negative, i.e., a loss in entropy generally accompanies exothermic adsorption. Thus, an increase in column temperature lessens retention. Surprisingly, the retention of C_{60} and C_{70} on CSP 1 increases when column temperature

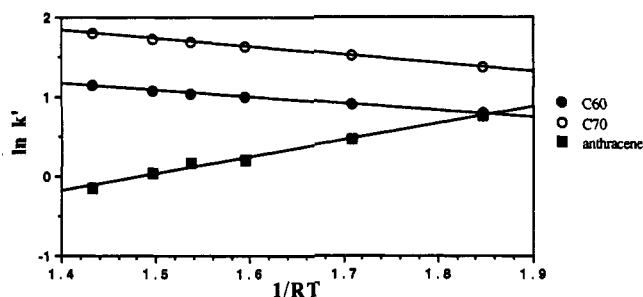


Figure 1. Effect of temperature on retention of C_{60} , C_{70} , and anthracene. Column = Regis (*R*)-*N*-(3,5-dinitrobenzoyl)-phenylglycine (CSP 1, 4.6 mm i.d. \times 25 cm length); mobile phase = 10% dichloromethane in hexane; flow rate = 2.00 mL/min; void time determined by injection of 1,3,5-tri-*tert*-butylbenzene;⁷ all samples dissolved in mobile phase prior to injection. $\Delta H C_{60}$ = +0.82 kcal/mol; $\Delta S C_{60}$ = +4.6 cal/mol K; $\Delta H C_{70}$ = +1.0 kcal/mol; $\Delta S C_{70}$ = +6.4 cal/mol K; ΔH anthracene = -2.1 kcal/mol; ΔS anthracene = -6.2 cal/mol K.

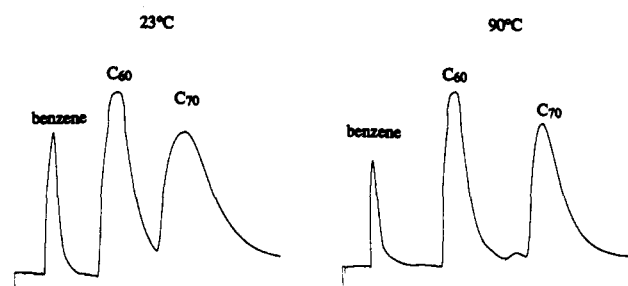


Figure 2. Preparative separation of C_{60} and C_{70} carried out at room temperature and 90 °C. Column = Regis (*R*)-3,5-(dinitrobenzoyl)phenylglycine (CSP 1, 21.1 mm i.d. \times 25 cm length); flow rate = 9 mL/min; mobile phase = hexane; sample = 500 μ L injection of a 6 mg/mL benzene solution of C_{60} and C_{70} .

is increased (Figure 1). Thermodynamic parameters obtained from the van't Hoff plots for C_{60} and C_{70} reveal positive enthalpy and entropy values, i.e., a gain in entropy accompanies endothermic adsorption. This unusual temperature dependence is observed in a variety of mobile phases with several different π -acidic and π -basic stationary phases and with silica. Polynuclear aromatic dopants such as anthracene and naphthalene behave normally under the same conditions.

Positive values for ΔH and ΔS of adsorption usually indicate that some association detrimental to analyte adsorption is being reversed as temperature is raised.⁸ While further work would be required to understand the origin of this unusual behavior, it can be exploited to improve preparative separations. Elevated column temperature decreases the retention for benzene, increases both the solubility and the retention of C_{60} and C_{70} , and improves bandshapes (Figure 2). In a pumped system, column pressure elevates the boiling points of the eluents, permitting their use at temperatures above their normal boiling points. While the use of elevated temperatures improves the separation process, the purification of C_{60}/C_{70} on CSP 1 is still difficult owing to the insolubility of the

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material. Only about 100 mg of crude C_{60}/C_{70} mixture has been successfully resolved per run on a 2 in. i.d. \times 4 ft length preparative column containing CSP 1 bonded to 60 μ m irregular silica particles. Normally, this column will separate 20 g per run of a soluble racemate having a separation factor similar to that of the C_{60}/C_{70} mixture.

Acknowledgment. We are grateful to Professor John Shapley and Dr. Scott Koefod for providing the crude mixture of C_{60} and C_{70} used in this study. This work was supported by grants from the National Science Foundation and Department of Education Advanced Opportunities in Chemistry Graduate Fellowship.

Articles

A Comparison of (Chloromethyl)- and (Iodomethyl)zinc Cyclopropanation Reagents

Scott E. Denmark* and James P. Edwards

Roger Adams Laboratory, Department of Chemistry, University of Illinois, Urbana, Illinois 61801

Received July 2, 1991

A study comparing the rate of cyclopropanation of a range of olefins using (chloromethyl)- and (iodomethyl)zinc reagents is described. The (chloromethyl)zinc reagent derived from diethylzinc and chloriodomethane is generally more reactive than the (iodomethyl)zinc analogue. The use of 1,2-dichloroethane as the solvent for these reactions was shown to be a crucial factor necessary to achieve clean, rapid, high-yielding cyclopropanations. The well-known directing effect of proximal oxygen substituents on the stereochemical outcome of "Simmons-Smith" cyclopropanations was shown to hold for the (chloromethyl)zinc reagent as well. The diethylzinc/chloriodomethane reagent system in 1,2-dichloroethane should prove to be a valuable alternative to traditional (iodomethyl)zinc-based cyclopropanation reagents.

Introduction and Background

The discovery¹ that treatment of an ethereal suspension of a zinc/copper couple with diiodomethane generates an organometallic reagent² that transforms olefins into cyclopropanes was a watershed event in cyclopropane chemistry. This is evidenced not only by the impressive array of olefins successfully cyclopropanated by this procedure³ (or the subsequent improvements and modifications^{4,5}), but also by its acceptance as a primary method of synthesizing cyclopropanes for both mechanistic and synthetic efforts.^{3,6} Although the initial method of preparation of the zinc/copper couple was cumbersome, several synthetically more accessible and reproducible methods quickly followed.⁴ Notable among these are the organozinc reagents prepared from either Et_2Zn/CH_2I_2 ⁵ or ZnI_2/CH_2N_2 .⁷ The species generated by these methods

displayed similar reactivity toward olefins as the classic Simmons-Smith reagent. That all of these reagents possess, at least in part, the "(iodomethyl)zinc" (ICH_2ZnX) moiety was firmly established by chemical transformations.^{3,7}

The synthetic utility of the Simmons-Smith cyclopropanation derives from the following characteristics: (1) stereospecificity (strict retention of olefin geometry), (2) generality with regard to olefin structure, and (3) the syn-directing effect of hydroxyl and ether functions.^{8,9} Recent reports of highly diastereoselective cyclopropanations of olefins bearing recoverable¹⁰ or nonrecoverable¹¹ chiral auxiliaries which utilize Simmons-Smith

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