Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

Effect of Position of Substitution on the Separation Behavior of Deuterated Toluene

Donald Macnaughtan Jr.[ab]; L. B. Rogers[a]
[a] DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY LAFAYETTE, INDIANA [b] Chemistry Department, University of Illinois, Urbana, Illinois

To cite this Article Macnaughtan Jr., Donald and Rogers, L. B.(1972) 'Effect of Position of Substitution on the Separation Behavior of Deuterated Toluene', Separation Science and Technology, 7: 4, 307 — 318
To link to this Article: DOI: 10.1080/00372367208055575
URL: http://dx.doi.org/10.1080/00372367208055575

SEPARATION SCIENCE, 7(4), pp. 307–318, 1972

Effect of Position of Substitution on the Separation Behavior of Deuterated Toluene*

DONALD MACNAUGHTAN, JR.,† and L. B. ROGERS

DEPARTMENT OF CHEMISTRY
PURDUE UNIVERSITY
LAFAYETTE, INDIANA 47907

Abstract

The position and number of deuterium atoms substituted onto the toluene molecule was found to affect its separation behavior on a silver nitrate-water column. Substitution on the ring affected the capacity ratio substantially while substitution on the methyl group had no measurable effect. At the same time, the separation behaviors of benzene and perdeuterobenzene were examined using several other salt solutions and polar liquids as possible stationary phases.

INTRODUCTION

A number of separations of deuterated species from normal species have been accomplished using both packed and open tubular columns. These include small hydrocarbons such as the alkanes (*1–6*), alkenes (*1, 3, 7, 8*), and benzene (*8*). In addition, small polar deuterated species such as methanol, ethanol, and acetonitrile have been separated (*3*).

* Supported in part by the U.S. Atomic Energy Commission under Contract AT(11-1)-1222.

† Present address: Chemistry Department, University of Illinois, Urbana, Illinois 61801.

Tritiated methanes have also been isolated (*2*, *9*). In all cases, low-molecular-weight compounds were probably selected because of the relatively large change in molecular weight upon deuteration and because they are more readily prepared pure.

The observed behavior for isotopic separations generally shows that at low temperatures the hydrogen species elutes first while at higher temperatures the most deuterated species elutes first. At intermediate temperatures there is a cross-over point where no separation occurs. (Also, at relatively high temperatures there is little separation). The inversion point for methane-d_4 is 133°K (*1*), and the inversion point generally increases with the molecular weight of the pair.

The separation behavior has been explained on the basis of changes in the polarizability (*1*, *7*, *10*) and in the vapor-pressure ratio with temperature (*11*) according to the relationship:

$$\ln P/P' = (B/T) - (A/T^2) \tag{1}$$

where P and P' are the vapor pressures of the normal and deuterated species, respectively, A and B are constants, and T is the Kelvin temperature. In addition, specific interactions of the compound with the column material may be confounded with the above effects. This has been noted for silver nitrate columns used in separating olefins (*7*, *8*) where a specific interaction, complexation, is responsible for separating the olefins in the normal elution order even though the vapor pressures favor separation in the opposite way.

The purpose of the present study was to determine the separation behavior of toluene and deuterotoluenes including d_2(ring), d_3(methyl), and d_8 species. Hence, it was possible to examine the effect of the position of deuterium substitutions using the partially deuterated toluenes. In preliminary experiments we confirmed earlier work on the separation of benzene and benzene-d_6 (*8*) and the use of water as a liquid phase (*12*). That study was extended so that comparisons could be made with toluene behavior. Other column materials, including salts and polar liquids, were also investigated for separations of aromatic compounds.

EXPERIMENTAL

Apparatus

The high-precision gas chromatograph has been described previously (*13*). However, high-precision temperature control was not possible at

the temperatures used, so control was closer to ±0.1°C than to ±0.02°C.

A Digital Equipment Company PDP 11/20 was used off-line for data processing and for simulations.

Reagents

The deuterated species, 99.5% benzene-d_6 (Stohler Isotope, Rutherford, New Jersey), 99% toluene-d_8 and 98% trideuteromethylbenzene (toluene-d_3) (Diaprep Inc., Atlanta, Georgia), and 98% *o*-dideuterotoluene (toluene-d_2) were used as obtained. The toluene-d_2 was obtained from Diana Darling of this department who prepared the material by refluxing *p*-nitrotoluene with 95% D_2SO_4 (*14*), producing the *o*-deutero form. The nitro group was then removed by reduction with Sn and HCl, and formation of the diazonium salt using sodium nitrite. This was replaced with hydrogen using H_3PO_2 to give toluene-d_2. The benzene (J. T. Baker) and toluene (Mallinckrodt) were reagent grade.

Praseodymium acetate, praseodymium oxide, praseodymium sulfate, europium acetate, and europium sulfate (all from Bradford Scientific, Marblehead, Massachusetts) were 99.9% pure. The europium oxide (Alfa Inorganics, Beverly, Massachusetts) was 99.99%. All the compounds were used as obtained. The chlorides were prepared by dissolving the appropriate oxide in hydrochloric acid and drying to the salt at 120°C. The silver nitrate, copper(II) sulfate, and lithium chloride were reagent grade.

Fluorolube, grade LG160 (Hooker Chemical, Niagara Falls, New York), IH, 1*H*,9*H*-hexadecafluoro-1-nonanol (DuPont), and Kel-F wax (Applied Science Laboratories, State College, Pennsylvania) were used as partitioning liquids. Support materials were Davison Silica Gel, 100/200 mesh, and Chromosorb P, 60/80 mesh.

All the materials listed in Table 1 were coated on 60/80 mesh Chromosorb P. The salt packings were wet with 10 to 30% water by weight, and water-saturated carrier gas was used unless noted otherwise.

The carrier gas was 99.99% pure Airco helium. Airco hydrogen and Linde compressed air were used for the flame-ionization detector. Each of these gases was passed through a 4A molecular sieve trap before use. Airco nitrogen was used as received for value actuation.

Procedures

Chromatography. Liquid phases were coated on the support material after dissolving the liquid in an appropriate solvent and evaporating the

TABLE 1

The Separation Behavior of Benzene and Benzene-d_6 on Different Stationary Phases

Number	Stationary phase[a]	Column length (m)	k, benzene	a, $\frac{\text{benzene-}d_6}{\text{benzene } h_6}$	t,benzene-d_6 (sec)
1	25% $AgNO_3$[b]	2.5	26.5	1.070 ± .002	935
2	39% H_2O, 27°C	2.0	0.9	1.051 ± .008	90
	10°C	2.0	3.2	1.051 ± .005	195
	0°C	2.0	5.0	1.053 ± .003	280
3	5% Fluorolube[c]	2.7	5.3	1.030 ± .01	335
4	5% DV-8976,[c] 60°C	2.3	1.1	1.020 ± .01	55
5	20% LiF[c]	2.0	2.2	1.02 ± .01	80
6	20% LiF	2.0	1.6	1.01 ± .01	55
7	10% $LaCl_3$	2.0	0.4	1.04 ± .01	60
8	10% $Pr_2(SO_4)_3$	2.5	—	1.039 ± .002	101
9	10% $EuCl_3$	2.5	0.7	1.031 ± .004	88
10	20% $PrAc_3$	2.5	0.5	1.045 ± .004	70
11	20% $PrCl_3$	2.3	0.6	—	140
12	10% $CuSO_4$	2.5	0.6	1.043 ± .004	83

[a] Loading on Chromosorb P 60/80, and carrier gas saturated with water at the column temperature (27°C unless noted otherwise).

[b] Saturated solution in water at 27°C.

[c] Dry carrier gas and packing.

solvent by using a rotary evaporator. Salts were dissolved only in distilled water and any hydrolysis was ignored.

The amount of water left on the packing was controlled using either of two methods. In one, the water was evaporated from the stirred packing at about 70°C until the desired weight had been attained. In the second, the packing was dried completely at 70°C and the desired amount of water was added to the packing, mixed thoroughly, and allowed to stand in a closed container for 24 hr before packing the column. The amount of water in the packing was checked by first weighing the packing and drying it to constant weight in a 120°C oven.

The organic liquid-phase packings were placed in 1.54 mm i.d. × 1 m copper tubing while the aqueous salt packings were put into 2.2 mm i.d. × 2 m nylon tubing (Clippard Instrument Co., Cincinnati, Ohio). Packing was effected by attaching the tubing to a water aspirator and

funneling the packing into the open end while using an electric vibrator along the tubing. The ends were plugged with silanized glass wool (Analabs, Hamden, Connecticut).

The availability of sample injection and data acquisition, both under digital control, made it possible very quickly to obtain accurate values for the relative retention α by using short columns, 1–2 m long. When the separation was insufficient to permit accurate measurements to be made on a mixture, separate injections of each of the pure species were made at an interval that permitted adequate resolution while insuring that both species shared most of the time in the column. Thus a typical chromatographic precedure for determining separation parameters for a pair of samples involved runs of the individual compounds under specific column conditions to determine approximate retention times and peak widths. This allowed determination of the appropriate injection interval of the two samples and the delay time before which the chromatogram was not digitized. These times were then set on the digital controller, and the digitizing rate was set so that approximately 250 data points were taken across the peaks. The gas flow through the dilution flask was adjusted so that the first sample was cleared out before the second sample was injected. This was checked using a methane sample several times larger than normal and observing that the signal obtained upon making a second injection after the selected interval of time was less than 1% of the signal from the first injection.

The actual run involved injecting a sample into the dilution flask 5 sec before the sample valve was operated to inject a portion of it into the column. The delay insured a suitable sample concentration. After the first sample had been injected, the syringe was cleaned, and a second sample put into the dilution flask, again 5 sec before it was to be injected into the column. After the injection sequence was halted, the controller digitized the chromatogram at the preset time, and the system halted for next run. A sample that gave a resolution greater than 0.5 was run simply by making one injection of 1:1 mixture from the dilution flask.

All samples were injected into the dilution flask as gases. The approximate amount of each sample chromatographed was determined in a separate run by injecting 1 μl of a 0.1% solution of toluene (or benzene) in cyclohexane directly onto the column and adjusting the sensitivity until the peaks were of the same size as the injections from the dilution flask. Typical sample sizes of toluene ranged from 20 to 60 ng and benzene from 5 to 20 ng.

Calculations. Separation parameters were calculated using computer

processing of punched paper tape and, in some cases, by using measurements from chart paper using a 60 division-per-inch ruler. The retention time t was taken at the maximum and then corrected using the retention time t_0 of methane (assumed to be nonretained). The capacity ratio k and the relative retention α were determined in the usual way (*15*). The uncertainties in α shown in Table 1 reflect the uncertainties in measuring two retention times (and two k values).

The width w of the peak was assumed to be twice the peak width at one-half the peak height. The resolution R was calculated as

$$\mathrm{R} = \frac{(t_2 - t_1)}{(W_2 + W_1)/2} \tag{2}$$

where the subscripts refer to the peaks in their order of elution. Resolution squared per second was also calculated using the time for the maximum of the second peak.

For some runs in which mixtures were injected, resolution measurements were made from the chart paper by Kaiser's method as outlined by Schupp (*15*). The peak maxima were connected by line AB of Figure 1 and the heights CE and DE were measured, D being the minimum point between the peaks. The percentage (DE/CE) × 100 was determined. However, we preferred to relate this percentage to the corresponding resolution of Eq. (2). A plot of percentage vs. R (Fig. 2) was obtained from computer simulations. That resolution was found to agree

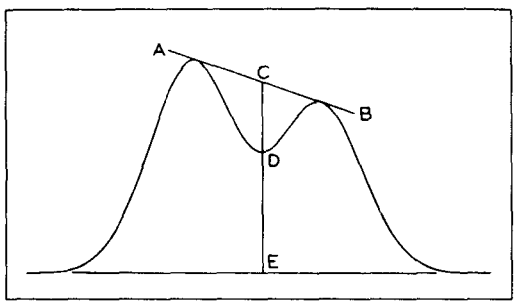

FIG. 1. Measurements for determining resolution of two peaks from height measurements.

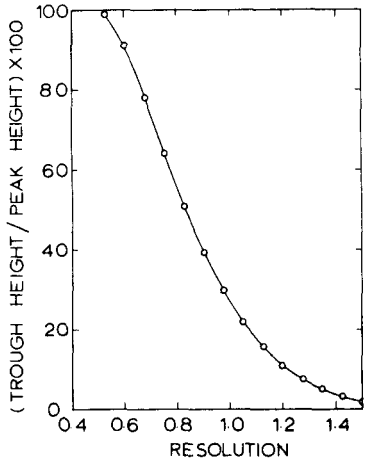

FIG. 2. Plot of $DE/CE \times 100$ vs. resolution from computer simulation.

to better than 1% with results from Eq. (2) if one peak height was not less than 80% of the other, even when the peaks were not the same width.

RESULTS

Benzenes

The separation behaviors of benzene and benzene-d_6 on columns using water and solutions of silver nitrate in water were generally found to be in good agreement with those reported by Wasik and Tsang (*8*). At temperatures from 0°C to room temperature, α remained essentially constant at 1.051 for water alone with the deuterated species being retained longer. However, on the silver nitrate columns, α increased with decreasing temperature as shown in Fig. 3. A decrease in α was also noted at a concentration of silver nitrate of 60% saturation (Fig. 4) which they (*8*) explained as a "salting-out" effect (*16*). This effect seemed to decrease for the saturated loadings, because α returned to the previous value.

In addition, use of water at loadings of 20% and higher was found to affect the HETP adversely (Fig. 5). Likewise, the ease of reproducing

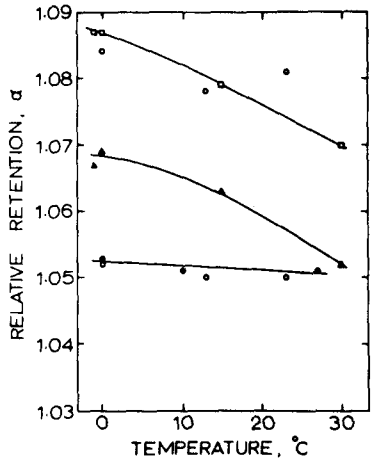

FIG. 3. Separation behavior of benzenes (h_6 and d_6), □, and toluenes (h_8 and d_8), △, on Column 1 in Table 1; and of benzenes (h_6 and d_6), ●, on Column 2 in Table 1. ○ represents data from Wasik and Tsang (*8*).

the packing, as measured by HEPT, became increasingly difficult above 10% water.

As expected, the amount of sample was found to affect the resolution substantially. A 1-ng sample of a 1:1 mixture had a resolution of 1.30, and a 10-ng sample gave 1.25 while a 100-ng sample gave 1.04.

In general, α for the benzene system improved at lower temperatures but did not improve substantially above 30% silver nitrate concentration nor above a 15% loading of liquid phase. The resolution also improved as the temperature decreased, paralleling α. However, the curves for R^2/sec obviously had maxima at faster flow rates and at higher temperatures than the resolution maxima (Fig. 6). As the temperature was increased, the retention time decreased more rapidly than the resolution, thus shifting the optimum value for R^2/t. In this work, values for R^2/t for a 10-ng sample of benzene and benzene-d_6 were about 30×10^{-4} sec^{-1} at 30°C under the conditions of Fig. 6.

Toluenes

It was possible to learn more about the separation behavior of deuterated aromatics by taking advantage of the availability of partially

deuterated toluenes. As shown in Fig. 7, three deuterium atoms in the methyl group, but none in the ring, did not produce an α that was measurably different from 1.00. However, the presence of two deuterium atoms in the ring (none in the methyl group) produced an α that appeared to fall on a straight line drawn through the values for zero and five deuterium atoms. The fact that the latter value was obtained using the perdeuterated species shows once again that one could not measure the effect of the three deuterium atoms in the methyl group.

Other Packings

From the data that have been presented, it is clear that, on silver nitrate columns, the separation behaviors of toluene and toluene-d_8 generally paralleled those of the benzene pair. However, α was not as large for the toluenes. For that reason the benzene system was used to test other possible column packings.

Generally, the salt columns showed little interaction with benzene as indicated by the lower capacity ratios compared to the silver nitrate columns. All of the α values for the benzene pair were less than the value on water alone. The retention times were also smaller. Therefore, the salts probably changed the surface structure of the water or caused a "salting-out" effect.

The fluorolube column was run normally with dry carrier gas, and it had some interaction with the benzene. However, the differences between the isomers was small. The other fluorocarbons posed some difficulty in that the higher molecular weight waxes had to be operated above their melting points, but the higher temperatures worked against the separa-

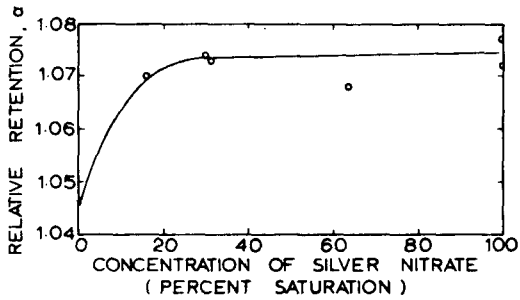

FIG. 4. The relative retentions at 27°C of benzene-h_6 and benzene-d_6 vs. the concentration of silver nitrate in the liquid phase.

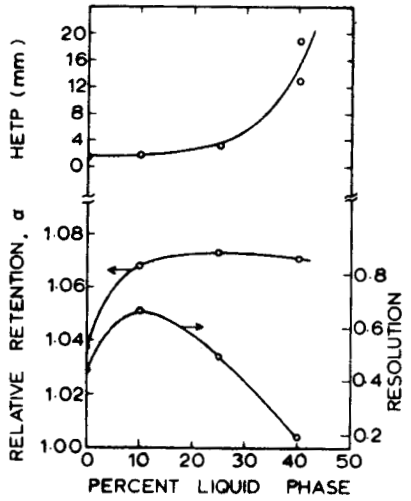

FIG. 5. The effect of percentage loading on column efficiency, (HETP), relative retention (α), and resolution at 27°C. Two-meter columns loaded with 10% silver nitrate solution.

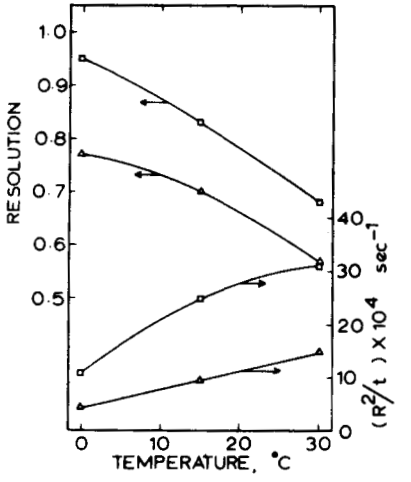

FIG. 6. Resolution of benzenes (h_6 and d_6), □, and toluenes (h_8 and d_8), △, vs. temperature using Column 1 in Table 1.

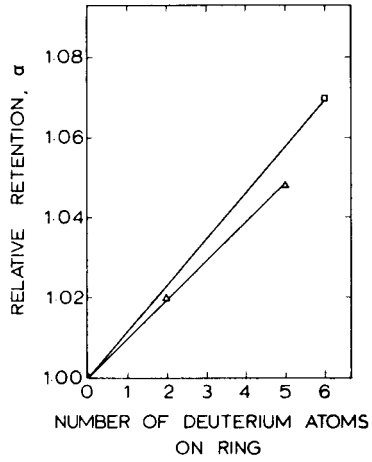

FIG. 7. The relative retentions of benzenes, □, and toluenes, △, vs. the number of deuterium atoms on the ring using Column 1 in Table 1.

tion. On the other hand, lower molecular weight fluorospecies tended to be too volatile.

DISCUSSION

To demonstrate the effect of water on the complexation reaction between silver nitrate and aromatics, one of the column packings was dried completely and the column repacked. Using dry carrier gas, a sample of benzene and benzene-d_6 was injected and it did not elute in 30 min. At this time the carrier was allowed to saturate with water, and this gas mixture was passed through the dry column. A second sample of the mixture was injected immediately after switching to the wet carrier gas. Both samples of benzene eluted close together at the expected retention time, indicating that the first sample had absorbed very strongly on the dry silver nitrate. However, a slight amount of water prevented total loss of sample on the active sites (*17*). The separation that was produced in each sample was the same, and was equivalent to that produced on the original wet column. This indicates a simple method for making efficient silver nitrate columns. The silver nitrate is added to the packing with enough water to cover all the material. This is dried quickly and completely with mixing. The dry material is easily packed and quickly equilibrates with a water-saturated carried gas to give an efficient column.

Examination of Fig. 7 shows that α for benzene containing five deuterium atoms on the ring should be greater than for the corresponding toluene if one assumes the linear relationship previously discussed. This indicates that the presence of the methyl group on the ring is lowering α. It is possible that this is a molecular-weight effect or that the electron density in the ring is being changed so that it affects the complexation with silver ion. Perdeuterofluorobenzene would be an appropriate compound to show which effect was predominant, providing the fluorine did not interact with the silver ion. The molecular weight of the methyl and fluoro groups is approximately equal, so α for fluorobenzene and fluorobenzene-d_5 should be the same as for the toluene pair if the molecular weight change is responsible for the different slopes in Fig. 7. However, if it is due to a change in the electron density in the ring, then the electron-withdrawing fluoro group should enhance the deuterium effect and give an α for the fluorobenzene pair that is larger than that for the toluene pair and possibly near or higher than the α for the benzene pair.

Acknowledgment

The help of Paul Taylor with some of the experimental work and some of the drawings is appreciated.

REFERENCES

1. F. Bruner, G. P. Cartoni, and A. Liberti, *Anal. Chem.*, *38*, 298 (1966).
2. F. Bruner, G. P. Cartoni, and M. Possanyini, *Ibid.*, *41*, 1122 (1969).
3. A. Di Corcia, D. Fritz, and F. Bruner, *J. Chromatogr.*, *53*, 135 (1970).
4. P. R. Norton, *J. Chromatogr. Sci.*, *8*, 411 (1970).
5. J. W. Root, E. K. C. Lee, and F. S. Rowland, *Science*, *143*, 676 (1964).
6. K. E. Wilzabach and P. Riesz, *Ibid.*, *126*, 748 (1957).
7. R. Cventanovic, F. Duncan, and W. Falconer, *Can. J. Chem.*, *41*, 2095 (1963).
8. S. P. Wasik and W. Tsang, *J. Phys. Chem.*, *74*, 2970 (1970).
9. K. Yang and P. Gant, *J. Amer. Chem. Soc.*, *86*, 5063 (1964).
10. A. Di Corcia and A. Liberti, *Trans. Faraday Soc.*, *66*, 967 (1970).
11. J. Bigeleisen, S. V. Ribnikar, and W. A. Van Hook, *J. Chem. Phys.*, *38*, 489 (1963).
12. B. Karger and A. Hartkopf, *Anal. Chem.*, *40*, 215 (1968).
13. J. E. Oberholtzer and L. B. Rogers, *Ibid.*, *41*, 1234 (1969).
14. R. N. Renaud, D. Kovachic, and L. C. Leitch, *Can. J. Chem.*, *39*, 21 (1961).
15. O. E. Schupp, "Gas Chromatography," in *Technique of Organic Chemistry*, Vol. 13 (E. S. Perry and A. Weissberger, eds.), Wiley (Interscience), New York, 1968, pp. 17–19 and 22.
16. C. Bighi, A. Betti, and F. Dondi, *J. Chromatogr.*, *39*, 125 (1969).
17. L. H. Plumer and H. K. Plumer, *Anal. Chem.*, *38*, 1652 (1966).

Received by editor October 8, 1971