

Table I. Effect of Calcium and Magnesium Ions on Determination of (Ethylenedinitrilo)tetraacetic Acid

	Additions, mmoles	(Ethylenedinitrilo)-tetraacetic acid	
		Added, mmoles	Found, mmoles
Ca ⁺²	1.0	0.040	0.042
	80.0	0.150 ^a	0.150 ^a
	100.0	0.040	0.041
	200.0	0.150 ^a	0.150 ^a
Mg ⁺²	1.0	0.040	0.042
	100.0	0.040	0.042

^a Ferric thiocyanate concentration used for analysis, 0.2mM.

is due to the fact that the stability constant of the iron-EDTA complex is greater than that of the alkali metal-EDTA complexes at pH 3.0. The results presented in Figure 1 show that orthophosphate and adenosine-5'-phosphate interfere with the formation of the red color of Fe(CNS)₃ at concentrations in excess of 0.5 mM. Adenosine di- and triphosphate interfere at concentrations of 0.05 mM.

The determination of micro amounts of EDTA by the usual titrametric methods, employing standard solutions of alkali metals (1), is frustrated by the presence of Ca⁺² and Mg⁺² in the sample. The procedure described herein, aside from being rapid, circumvents

this difficulty. The interference by phosphate and phosphate esters, however, limits the usefulness of the method.

LITERATURE CITED

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CHARLES J. PARKER, JR.

Department of Physiological Chemistry
Wayne State University College of
Medicine
Detroit, Mich.

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Separation of Isomeric Toluidines by Gas Liquid Partition Chromatography Using Ucon Oil as Stationary Phase

SIR: A stationary liquid phase that will resolve the individual toluidine isomers (*ortho*, *para*, and *meta*) suitable for quantitative analysis has not been reported. The separation of the toluidine isomers was discussed in the recent text of Burchfield and Storrs (1). Separation factors on several liquid phases that had been reported were too low to resolve all three isomers. Separation

was obtained by gas solid chromatography using a treated clay but the chromatograms were not suitable for quantitative analysis because of the marked peak asymmetry and tailing.

We studied several polyglycol-type stationary liquids and found that a polyalkylene glycol ether gave good resolution of all three toluidine isomers as shown in Figure 1.

EXPERIMENTAL

Column Preparation. Chromasorb W (trade name for nonacid-washed, flux-calcined diatomaceous silica) of 60- to 80-mesh was treated with alcoholic sodium hydroxide (6% NaOH on dried Chromasorb W) and the alcohol was evaporated (2). The desired weight of Ucon oil (50HB 5100) was dissolved in benzene, slurried with the sodium hydroxide-treated Chromasorb W and

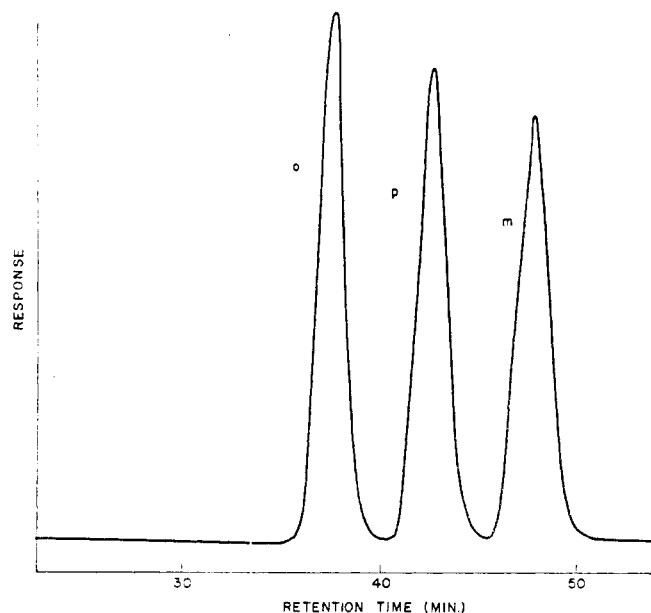


Figure 1. Separation of toluidines

o = *ortho*
p = *para*
m = *meta*

Conditions: Col., 10 ft., 3/16-in. o.d., 2.5% Ucon (50HB 5100); temp., 100° C.; flow, 60 ml./min.; sample size, 0.1 μ l.

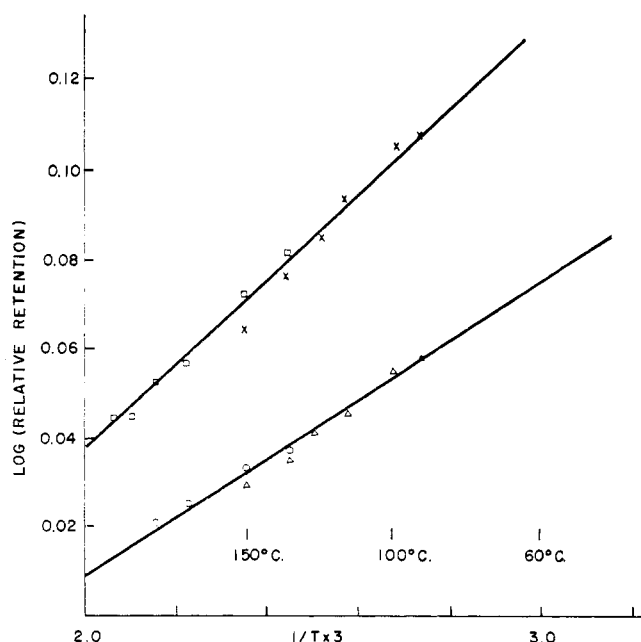


Figure 2. Separation vs. temperature

○ *para/ortho* (20% Ucon col.)
△ *para/ortho* (2.5% Ucon col.)
□ *meta/ortho* (20% Ucon col.)
× *meta/ortho* (2.5% Ucon col.)

Table I. Separation Factors of Toluidines

Stationary liquid	Relative retention time	
	<i>para/ortho</i>	<i>meta/para</i>
Polyglycol 2000 ^a	1.135	1.102
Carbowax 350 ^b	1.130	1.122
Carbowax 1500 ^c	1.055	1.182
Ucon 50HB 5100 ^d	1.130	1.125
Ucon LB 550X ^e	1.120	1.111
Silicone XF 1150 ^f	Not separated	1.145 (<i>m/o</i>)

^a Polypropylene glycol with average molecular weight of 2,000.

^b Methoxypolyethylene glycol.

^c Polyethylene glycol polymer.

^{d,e} Polyalkylene glycol ether.

^f High nitrile content silicone fluid.

the solvent removed in a rotary evaporator. A 10-foot, 3/16-inch o.d. stainless steel column was packed using vibration. Efficiency was 3,800 plates based upon the *m*-isomer using a 2.5% Ucon oil column.

Instrumentation. The F&M (609) hydrogen flame instrument was used.

Capillary Column. Liquid phases were screened using short 10-foot nylon tubing (about 1-mm. i.d.) which was coated by blowing through a 15% solution of the liquid phase in benzene.

RESULTS AND DISCUSSION

Separation factors at a column temperature of 100° C. for several of the glycol-type liquids and a polar silicone are tabulated in Table I. The Ucon oil (50HB 5100) and Carbowax 350 gave the best separation of the three toluidine isomers but the former had the ad-

vantage of much higher temperature stability than the latter. Figure 2 shows a plot of log *meta/ortho* and *para/ortho* retention times vs. reciprocal absolute temperature employing 2.5 and 20% Ucon (50HB 5100) loaded columns to cover the temperature range. The plot shows the improvement in separation factor at lower temperatures.

LITERATURE CITED

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J. S. PARSONS
J. C. MORATH

American Cyanamid Co.
Research Laboratories
Bound Brook, N. J. 08805

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A Spectrophotometric Study of the Reactions of *p*-Nitrotoluene in Basic Solution

SIR: Recently Russell and Janzen (1) have reported their electron spin resonance (ESR) data on the reactions of *p*-nitrotoluene (PNT) with potassium *t*-butoxide in *t*-butanol. We have also studied this system by ultraviolet (UV) and visible absorption spectrometry along with ESR spectrometry. These two techniques complement each other and provide additional information about this system.

All reactions were carried out in a dry box under nitrogen at room temperature. Solutions were thoroughly degassed. They were transferred to clean absorption cells which had been rinsed with a solution containing the red PNT free radical species and then with *t*-butanol. After they were tightly stoppered, the cells were removed from the dry box to the appropriate measur-

ing instrument. Typically, the concentration of PNT was $2.2 \times 10^{-4}M$ and that of potassium *t*-butoxide was 0.2M in *t*-butanol. At these concentrations, the solutions appeared red 15 minutes after the start of the reaction, and an ESR signal was first detected after about 20 minutes. A red color and an ESR signal persisted for up to two weeks under these conditions and no colored precipitate formed.

Molecular Absorption. All spectra were obtained on a Cary Model 11 recording quartz spectrophotometer using 1.00-cm. quartz cells. The spectral region from 260 to 700 mμ was observed in two scans, 260 to 380 mμ and 350 to 700 mμ, each taking between 2 and 3 minutes.

Spectral changes were complex (Figure 1) and no isosbestic points were observed;

however, definite, strong absorption bands appeared. They are summarized in Table I. Solutions which had reacted for 24 hours or more showed some slight cloudiness and a weak band at 352 mμ indicating a trace of *p,p'*-dinitrostilbene. However, the main absorption band at 517 mμ was strong enough to account for most of the material present in the solution. An ϵ value of 3.3×10^4 was calculated at this wavelength assuming that it represented the only species in solution.

Table II. Spectral Data on PNT and Related Compounds

(Solvent is *t*-butanol unless otherwise indicated)

Compound	λ_{\max} , mμ	ϵ
<i>p</i> -Nitrotoluene (PNT) ^a	272	8.3×10^3
<i>p</i> -Nitrobenzoic acid ^a	274 ^b	about 10^4
<i>p,p'</i> -Dinitrostilbene ^c	352	4×10^{4d}
<i>p,p'</i> -Dinitrobenzyl ^e	275	2.0×10^{4e}
	335	2.4×10^{4e}

^a Obtained from Matheson Coleman and Bell.

^b Potassium *t*-butoxide was present so this assignment is for the anion.

^c Prepared according to Russell and Moye (3) and characterized by infrared.

^d ϵ was determined in CHCl₃ at λ_{\max} = 357 mμ since dinitrostilbene is slightly soluble in *t*-BuOH.

^e ϵ values were determined in methanol at λ_{\max} = 277 mμ and 335 mμ since nitrobenzyl is slightly soluble in *t*-BuOH.

Table I. Summary of Spectral Data on PNT Reaction

Probable species	λ_{\max}	A	Time of max. intensity		Nature of ESR
			UV-visible	ESR	
PNT	272 mμ	1.8	0
Carbanion, $\text{CH}_2\text{C}_6\text{H}_4\text{NO}_2^-$	362	0.8	10 min.
Charge transfer complex	557 ^a	3.6	35 min.
Unidentified	300-310	1.0	1-2 hrs.
Free radical	538 ^a	2.0	3-4 hrs.	2-3 hrs.	Multi-line
Free radical	517 ^a	3.3	~24 hrs.	~24 hrs.	Single line

^a These absorption bands give the solution its red color. It is difficult, if not impossible, to distinguish between them visually.