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Equilibrium Distributions of the Dimethylethylbenzene and Methyldiethylbenzene Isomers

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Data on the equilibrium distribution of the dimethylethylbenzene and methyldiethylbenzene isomers are not available. Based on known equilibrium distributions of other polyalkylbenzenes, these equilibrium distributions may be predicted. Disproportionation of methylethylbenzene can produce these isomers. Disproportionation runs were made at different temperatures at varying space velocities to various degrees of equilibration. Under conditions where the methylethylbenzenes approach equilibrium, the trialkylbenzenes are at equilibrium, also. Thermodynamic equilibria were calculated from these data at two different temperatures. The experimental equilibrium data were in good agreement with the theoretical estimates.

DATA on the equilibrium distributions of the dimethylethylbenzene and methyldiethylbenzene isomers are not available. They were estimated from the equilibrium distributions (Table I) of similar compounds.

However, the ethyl group creates some steric hindrance. The effect of the steric hindrance on the equilibrium distribution can be approximated if one compares the ortho/para ratios of xylenes and methylethylbenzenes. At 327° C. these ratios are 0.96 and 0.49. The author applied this factor (0.5) for the corresponding dimethylethylbenzenes and methyldiethylbenzenes. Estimated equilibrium distributions are shown in Table II.

These distributions may be established experimentally by isomerization of the dimethylethylbenzene and methyldiethylbenzene isomers. However, these trialkylbenzenes are not readily available in pure form. In this paper, the author shows a new and simple method to obtain the equilibrium distribution of the dimethylethylbenzene and methyldiethylbenzene isomers using methylethylbenzenes which are readily available in pure form.

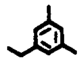
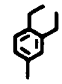
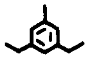
Disproportionation of the methylethylbenzenes gives

Table I. Equilibrium Concentrations[a] of C_8 and C_9 Alkylbenzenes in the Ideal Gas State at 327° C.

Xylenes, Mole %	
Ortho	22.9
Meta	53.3
Para	23.8
Ortho/Para	0.96
Methylethylbenzenes, Mole %	
Ortho	16.3
Meta	50.3
Para	33.4
Ortho/Para	0.49
Trimethylbenzenes, Mole %	
1,2,3-(Hemimellitene)	13.7
1,2,4-(Pseudocumene)	62.2
1,3,5-(Mesitylene)	24.1

[a] Calculated from data taken from reference (7).

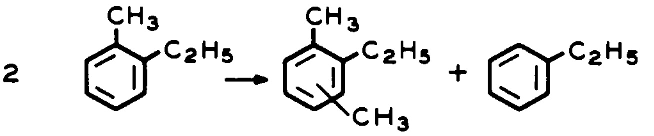
Table II. Estimated Equilibrium Concentrations of Dimethylethylbenzenes and Methyldiethylbenzenes

Trimethylbenzenes						
	1,2,3		1,2,4			1,3,5
Mole % at 327° C.	13.7		62.2			24.1
Corresponding dimethylethylbenzenes						
	1,2-3	1,3-2	1,2-4	1,3-4	1,4-2	1,3-5
Factor of steric hindrance caused by ethyl groups[a]	0.5	0.25	1.0	0.5	0.5	1.0
Estimated equilibrium distribution[b]	4.8	2.4	29.3	14.7	14.7	34.1
Corresponding methyldiethylbenzenes						
	1-2,3	1-2,6	1-2,4	1-2,5	1-3,4	1-3,5
Factor of steric hindrance caused by ethyl groups[a]	0.12	0.25	0.5	0.5	0.25	1.0
Estimated equilibrium distribution[b]	1.5	3	20	20	10	46

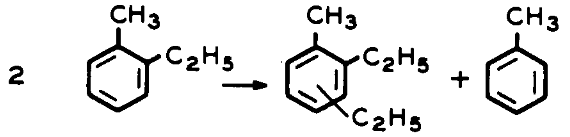
[a] The factor was derived from the difference between the ortho/para ratios of xylenes and methylethylbenzenes. See text. [b] Distributions were estimated by dividing the equilibrium concentration of the corresponding trimethylbenzene with the number of possible related structures (2 for 1,2,3-TMB; 3 for 1,2,4-TMB; and 1 for 1,3,5-TMB); multiplying the results with the steric hindrance factor, and normalizing to 100%. Example: 1-Methyl-2,4-diethylbenzene = 0.5 × 62.2/3 = 10.4; Normalized = 20%.

lower and higher molecular weight products. Two types of disproportionation are possible:

Methyl transfer, giving dimethylethylbenzenes and ethylbenzene:



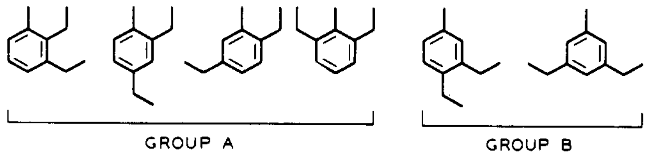
Ethyl transfer, giving methyldiethylbenzenes and toluene:



The reactions are catalyzed by Friedel-Craft type catalysts. The mechanism most probably involves 1,1-diphenylalkane intermediates. Evidence for this mechanism was presented by Streitwieser and Reif (*8*).

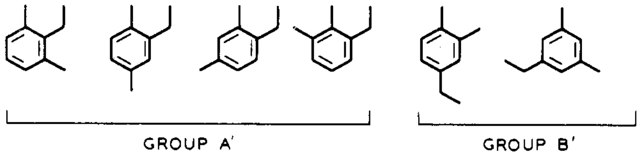
FORMATION OF ISOMERS

There are six methyldiethylbenzene isomers.



The isomers in group A can be formed directly from 1-methyl-2-ethylbenzene by disproportionation through ethyl transfer. In practice, however, 1-methyl-2,3-diethylbenzene and 1-methyl-2,6-diethylbenzene were not observed in the reaction product. (Substitution of an ethyl group next to two other alkyl groups is sterically hindered.) The isomers in group B (1-methyl-3,4-diethylbenzene and 1-methyl-3,5-diethylbenzene) require either isomerization of 1-methyl-2-ethylbenzene before the ethyl transfer or isomerization of an isomer from group A. Such isomerization reactions are well known and usually catalyzed by acids (*4, 5, 6*). The reaction probably proceeds by protonation of the aromatic ring (*1, 3*).

The situation is similar with the six possible dimethylethylbenzene isomers.



Here we observed all four group A′ isomers. The isomers which cannot be formed directly from 1-methyl-2-ethylbenzene by disproportionation through methyl transfer (group B′) are 1,2-dimethyl-4-ethylbenzene and 1,3-dimethyl-5-ethylbenzene.

DISCUSSION

One aspect of any equilibrium study is to make sure that equilibrium conditions have been achieved. This work is concerned with the isomers which cannot be formed directly from 1-methyl-2-ethylbenzene by disproportionation (groups B and B′). If the isomerization which is needed to produce these isomers is faster than the rate of methylethylbenzene equilibration, and if conditions are chosen sufficient for the methylethylbenzenes to approach equilibrium, then the trialkylbenzenes will be at equilibrium, too.

The author reacted 1-methyl-2-ethylbenzene over commercially available silica-alumina cracking catalysts. Reaction conditions and catalysts were varied to ensure different levels of conversion (Table III). The reaction products contained the methylethylbenzene isomers, toluene, ethylbenzene, the dimethylethylbenzene, and the methyldiethylbenzene isomers. The product was analyzed by vapor phase chromatography.

The relative amount of the methyldiethylbenzene isomers which cannot be formed directly from 1-methyl-2-ethylbenzene (group B) was related to the extent of methylethylbenzene isomerization—Table IV and Figure 1. The same relationship was found with the dimethylethylbenzenes—Table IV and Figure 2.

Alkyl migration-type isomerization of the dimethylethylbenzenes and methyldiethylbenzenes was faster than that of the methylethylbenzenes. Initial isomerization rates were determined graphically from Figures 1 and 2. Relative initial

Table III. Isomerization of the Disproportionation Products of 1-Methyl-2-ethylbenzene over Silica-Alumina Cracking Catalyst[a] at Atmospheric Total Pressure in Hydrogen Diluent

Experiment number	1	2	3	4	5	6	7	8	9	10	11	12
Temperature, ° C.	204	315	400	400	400	400	400	400	315	400	400	400
Liquid hourly space velocity	8	8	32	16	8	3.2	8	8	8[d]	8[d]	8[d]	4
Hydrocarbon partial pressure, atm.	0.25	0.25	0.25	0.25	0.25[e]	0.10[e]	0.25	0.25	0.25	0.25	0.25	0.33[e]
Total dimethylethylbenzenes, mole %	0.003	0.034	0.020	0.035	0.12	0.10	0.068	0.075	0.08	0.13	0.15	0.39
Total methyldiethylbenzenes, mole %	0.20	0.36	0.15	0.25	0.70	0.50	0.46	0.54	1.37	0.88	1.10	2.10
Isomerized methylethylbenzenes, % of total methylethylbenzenes	0.24	4.37	9.26	14.9	18.2	18.9	27.8	29.4	45.7	56.5	67.6	80.0
Isomerized dimethylethylbenzenes, % of total dimethylethylbenzenes[b]	0	8.9	18.4	26.0	30.0	32.5	35.7	37.2	47.4	56.0	54.6	59.3
Isomerized methyldiethylbenzenes, % of total methyldiethylbenzenes[c]	1.15	20.1	28.8	37.0	39.1	40.6	47.3	46.2	56.3	53.2	55.5	56.7

[a] The catalyst was a commercial synthetic silica-alumina, containing 10 weight % Al_2O_3, 90 weight % silica, 0.1 weight % Na_2O. Its B.E.T. N_2 adsorption surface area was 340 $m.^2/g$. [b] Direct Products = 1,2-DiMe-3 EB + 1,3-DiMe-2-EB + 1,3-DiMe-4-EB + 1,4-DiMe-2-EB. Isomerized Products = 1,2-DiMe-4-EB + 1,3-DiMe-5-EB. [c] Direct Products = 1-Me-2,4-DiEB + 1-Me-2,5-DiEB. Isomerized Products = 1-Me-3,4-DiEB + 1-Me-3,5-DiEB. [d] Fresh catalyst. [e] Helium diluent.

Table IV. Observed Equilibrium Concentrations of Dimethylethylbenzene and Methyldiethylbenzene Isomers[a]

Temperature, ° C.	315									400				
Run number	15	16	17	18	19	20	21	22	Average	11	12	13	14	Average
Dimethylethylbenzenes														
1,2-Dimethyl-3-ethylbenzene	3.17	3.06	3.10	3.00	3.12	3.33	3.52	3.13	3.18	4.50	4.95	3.83	...	4.43
1,2-Dimethyl-4-ethylbenzene	21.57	18.51	20.06	20.58	20.11	21.68	22.67	22.20	20.92	24.87	27.39	22.44	...	24.90
1,3-Dimethyl-2-ethylbenzene	1.79	1.74	1.61	1.85	1.87	1.96	1.80	2.33	1.87	2.06	1.18	3.12	...	2.12
1,3-Dimethyl-4-ethylbenzene	15.72	16.82	17.22	16.73	16.41	16.42	15.79	16.29	16.43	16.87	16.52	17.32	...	16.90
1,3 Dimethyl-5-ethylbenzene	34.95	34.75	31.88	33.38	34.16	32.44	33.98	33.76	33.66	29.75	31.86	32.67	...	31.43
1,4-Dimethyl-2-ethylbenzene	22.80	25.12	26.13	24.46	24.33	24.14	22.24	22.29	23.94	21.95	18.10	20.62	...	20.22
Methyldiethylbenzenes[b]														
1-Methyl-2,4-diethylbenzene	20.27	21.34	20.73	21.15	21.30	19.97	19.95	21.00	20.71	21.57	20.60	23.12	21.18	21.62
1-Methyl-2,5-diethylbenzene	21.29	21.81	21.17	22.10	22.13	20.82	21.48	22.29	21.64	22.86	22.71	24.31	23.53	23.35
1-Methyl-3,4-diethylbenzene	9.82	10.15	9.47	10.19	10.51	9.73	10.35	9.56	9.97	11.12	10.73	11.92	11.65	11.36
1-Methyl-3,5-diethylbenzene	48.62	46.70	48.63	46.56	46.06	49.48	48.22	47.15	47.68	44.45	45.96	40.65	43.64	43.67
Isomerized methylethylbenzenes,[c] per cent of total methylethylbenzenes	76.7	68.5	65.8	71.8	73.7	74.4	80.1	77.3	...	67.6	80.0	74.0	81.0	...

[a] Reaction conditions in all the experiments but No. 12 were: A liquid hourly space velocity of 8 and a hydrocarbon partial pressure of 0.25 atmosphere. In experiment No. 12 the liquid hourly space velocity was 4, and the hydrocarbon partial pressure was 0.33 atmosphere. [b] 1-Methyl-2,3-diethylbenzene and 1-methyl-2,6-diethylbenzene were not observed. [c] Meta- and para-methylethylbenzenes.

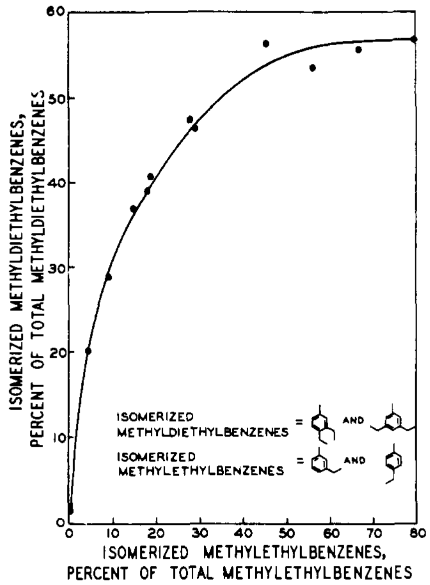


Figure 1. Distributions of methyldiethylbenzene isomers

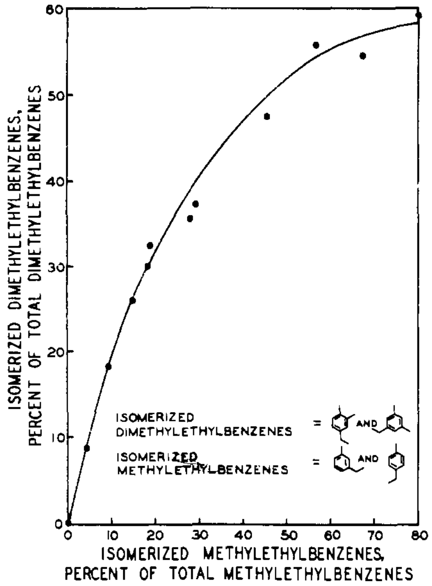


Figure 2. Distributions of dimethylethylbenzene isomers

isomerization rates of methylethylbenzenes, dimethylethylbenzenes, and methyldiethylbenzenes are in the ratio of 1 to 2.5 to 5. This difference in rates may be due to statistical factors—there are three alkyl groups which can move instead of two—or to the difference between the stabilities of protonated trialkylbenzenes and dialkylbenzenes. This type of isomerization is believed to be catalyzed by Brønsted acid sites. The first step of the reaction is the protonation of the aromatic ring. The stability of the benzonium ion increases with increasing number of alkyl substitutents owing to hyperconjugation. Thus, ring protonation of trialkylbenzenes is easier than that of the dialkylbenzenes.

The faster isomerization rate of the methyldiethylbenzenes relative to the dimethylethylbenzenes may be explained by the greater mobility of the ethyl groups than that of the methyl groups.

RESULTS

Calculated (7) equilibrium compositions of the methylethylbenzene isomers are:

	315° C.	400° C.
Ortho	15.7	17.7
Meta	50.3	50.2
Para	34.0	32.1

In several of our experiments equilibration of the methylethylbenzenes was complete, or nearly complete. In these experiments (Table IV), we should expect equilibrium distributions of the dimethylethylbenzene and methyldiethylbenzene isomers, also. The estimated equilibrium distribution patterns are in good agreement with the average experimental isomer distributions, especially in the case of the methyldiethylbenzenes (Table V). The 315° C. data are averages of eight experiments; the 400° C. data are averages of four experiments.

From these experimental equilibrium compositions one can calculate the relative free energies of the various isomers (Table V). Free energies were given relative to the most stable isomer—i.e., 1,3-dimethyl-5-ethylbenzene for the dimethylethylbenzenes, and 1-methyl-3,5-diethylbenzene for the methyldiethylbenzenes.

EXPERIMENTAL

1-Methyl-2-ethylbenzene was purchased from Columbia Organic Chemicals Co., Columbia, S.C. Purity = 99.77 mole

Table V. Equilibrium Distribution of the Dimethylethylbenzene and Methyldiethylbenzene Isomers

	Equilibrium Distribution			Relative Free Energy, Kcal./Mole	
	Observed		Estimated		
Temperature, ° C.	315	400	327	315	400
	Dimethylethylbenzenes, %				
1,2-Dimethyl-3-ethylbenzene	3.2	4.4	4.8	2.75	2.64
1,2-Dimethyl 4-ethylbenzene	20.9	24.9	29.3	0.56	0.32
1,3-Dimethyl-2-ethylbenzene	1.9	2.1	2.4	3.36	3.62
1,3-Dimethyl 4-ethylbenzene	16.4	16.9	14.7	0.84	0.83
1,3-Dimethyl-5-ethylbenzene	33.7	31.5	34.1	0	0
1,4-Dimethyl-2-ethylbenzene	23.9	20.2	14.7	0.40	0.59
	Methyldiethylbenzenes, %				
1-Methyl-2,3-diethylbenzene	...	...	1.5	...	...
1-Methyl-2,4-diethylbenzene	20.7	21.6	20	0.98	0.94
1-Methyl-2,5-diethylbenzene	21.6	23.3	20	0.93	0.84
1-Methyl-2,6-diethylbenzene	...	...	3	...	...
1-Methyl-3,4-diethylbenzene	10.0	11.4	10	1.83	1.80
1-Methyl-3,5-diethylbenzene	47.7	43.7	46	0	0

% 1-methyl-2-ethylbenzene, 0.15% 1-methyl-3-ethylbenzene, 0.08% xylenes, and other light hydrocarbons. Sulfur content was 0.3 p.p.m.

Disproportionation Reaction. The author used a continuous flow-type tubular reactor, consisting of a 50-cm. long, 0.635-cm. O.D. stainless steel tube. The tube held 0.5 ml. of 100 to 200 mesh catalyst. The catalyst used in most of the experiments was a commercial synthetic silica-alumina cracking catalyst. The catalyst contained 10 weight % alumina, 90 weight % silica, and 0.1 weight % Na_2O. The B.E.T. nitrogen surface area of the catalyst was 340 $m.^2$ per gram. The experiments were carried out at atmospheric pressure with a hydrogen diluent at a hydrogen-to-methylethylbenzene mole ratio of 3. Liquid feed rate was varied to obtain different conversion levels. The author collected the reaction products in an acetone–dry ice-cooled condenser. Reaction periods were 65 minutes long.

Product Analysis. A 300-foot long, 0.02-inch I.D. capillary column was used for the analyses of the liquid products. The column was packed with Ucon LB550-X polypropylene glycol. Sample sizes were between 2 and 5 μl. The analytical procedure is described in detail by Baumann and Csicsery (*2*).

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Enthalpies of Solution and Formation of Some Uranium Oxides

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The enthalpies of formation of U_4O_9, β-U_3O_7, and γ-UO_3 have been determined to be $\Delta H_{f\ 298.15^\circ K.}$ = −1078.1 ± 3.6, −818.4 ± 2.8, and −292.3 ± 1.4 kcal. per mole, respectively. The method used consisted of combining the known enthalpies of formation of $UO_{2.028}$ and U_3O_8 with data obtained from enthalpy of solution measurements of samples of U_4O_9, U_3O_7, and U_3O_8 and of mixtures of $UO_{2.028}$ and $UO_{2.993}$ of corresponding compositions. An aqueous 0.057*M* $Ce(SO_4)_2$–1.5*M* H_2SO_4 solution was used as the solvent.

URANIUM forms many oxides, including UO_2, U_4O_9, U_3O_7, U_3O_8, and UO_3, of which several may exist in more than one polymorphic form. In addition, wide homogeneity ranges exist for some of these oxides at moderately elevated temperatures. The enthalpies of formation of the uranium oxides are of considerable practical and theoretical interest. This paper presents the results of some work on the measurement of the enthalpies of solution of several uranium oxides, and oxide mixtures, in aqueous $Ce(SO_4)_2$–H_2SO_4 solutions, from which, given the enthalpies of formation of UO_2 and U_3O_8, the enthalpies of formation of U_4O_9, U_3O_7, and UO_3, can be calculated.

A review of the phase diagram and the enthalpies of formation of the uranium oxides, as of 1962, has been given by Rand and Kubaschewski (*9*). Table I lists their assessed values along with some recently determined experimental values, including the results reported here.

EXPERIMENTAL

The method involved measurement in a solution calorimeter of the differences in the enthalpies of solution obtained when U_4O_9, U_3O_7, or U_3O_8 was dissolved in 1.5*M* H_2SO_4 which was also 0.057*M* in $Ce(SO_4)_2$ and the enthalpy change obtained when corresponding mixtures of $UO_{2.028}$ and $UO_{2.993}$ were dissolved in the same solvent. The details of the solution calorimeter, its operation, and the procedures have been described (*5*). Briefly, the calorimeter is an isothermal solution calorimeter whose environmental temperature may be kept constant at any setting between 23° and 33° to within 0.001° in an 800-liter thermostatically controlled bath. The vacuum-jacketed, silver-bodied, platinum-lined calorimeter reaction vessel has a volume of ~450 cc., a thermal leak modulus of 0.005 per minute, and a heat capacity of 420 cal. per degree.

Within the reaction chamber are a heater, a thermistor, a borosilicate glass rod to which is attached a platinum stirrer, and a glass sample bulb. The heater consists of a 15.24-cm. length of 0.64-cm. O.D. platinum tubing, the lower end gold soldered, the upper end sealed to glass tubing which extends through the calorimeter lid and carries the heater leads. The platinum tubing contains 23 ohms of bifilarly wound, helically coiled, silk-covered manganin wire with leads to measure the voltage drop, located at the solution level. A Fenwal 2300-ohm thermistor is used as the sensing element to measure temperature differences up to 1.6° to within 0.0001°. A Brown recorder was modified to an automatic-changing, multiscale, self-balancing Wheatstone bridge, whose arm position is an indication of the resistance of the thermistor.

The energy equivalent is determined by passing a current from a precision voltage-regulated supply through the calorimeter heater and a 0.1-ohm standard resistor in series and measuring the voltage drops using a Rubicon Type