

THE ETHYLATION OF BENZENE. THE COURSE OF THE REACTION¹

E. M. MARKS, J. M. ALMAND, AND E. EMMET REID

Received August 7, 1943

From the preparative standpoint the ethylation of benzene has been well taken care of by a long line of investigators. Ethylated benzenes may be obtained readily and in good yields by introducing the appropriate amounts of ethylene into benzene in the presence of aluminum chloride. The same may be accomplished, though much less economically, with ethyl chloride. It has been tacitly assumed that the proportions of the products depend only on the amounts of the reactants put in; we find that this is far from being the case.

The purpose of the present investigation was to throw light on the mechanism of the reaction by a quantitative study of the alteration of its course by changes of the conditions. This required accuracy of an entirely different order in the determination of the products. In every run the two layers were separated and the hydrocarbons in each determined by fractionation in stills which gave results reproducible to within 1%. The percentage of the symmetrical isomer was determined in each of the triethylbenzene fractions. For preparation purposes the composition of the top layer, which is usually about nine-tenths of the product, is important. The lower catalytic layer can be used over again. Incidentally, from the data given, favorable conditions for obtaining any desired ethylated benzenes can be selected.

The normal course of the ethylation. Before studying the effects of changes in the reaction conditions, it was necessary to obtain a comprehensive picture of the formation and disappearance of the various ethylated benzenes, as ethylene is added under what may be called normal conditions, 268 cc. of ethylene per minute per mole of benzene, stirring at 7,500 r.p.m., 75°, and 13 moles of benzene to 1 of aluminum chloride. After a run is well started the absorption of ethylene is complete but at first some escapes and carries benzene with it. Hence the ethylene-benzene ratio has been calculated from the products. The results of runs in which from 1 to 5 moles of ethylene were added are in Table I. The line "E" shows the percentage distribution of the ethylene. The lines "T" and "B" give the molar percentages of the various ethylated benzenes in the top and bottom layers. The last column, "Sym.," shows the percentage of the 1,3,5-triethylbenzene in the tri-fraction, the remainder being the unsymmetrical. The results are shown in Fig. 1, which was constructed by drawing smooth curves through the known points and correcting these by trial so that at any point the moles of the products will add up to 100% and the moles of ethylene in them will equal the moles introduced. The result is an approximation, but the general picture is substantially correct for this set of conditions. The maxima for the various ethylation products correspond roughly to the amounts of ethylene put in but are at very different heights. The remarkable

¹ Taken from dissertations of E. M. Marks and J. M. Almand.

thing is the large amount of the hexaethyl that is formed in the early stages of the ethylation. Of the first mole of ethylene 18% goes to form hexa- and only 27% to the mono-ethyl. The early appearance of the hexaethyl has been noted

TABLE I

DISTRIBUTION OF ETHYLENE WHEN VARIOUS AMOUNTS ARE INTRODUCED INTO 1 MOLE OF BENZENE AND THE COMPOSITIONS OF THE TOP AND BOTTOM LAYERS IN MOLE-PERCENTAGES. ALSO THE PERCENTAGE OF THE 1,3,5-ISOMER IN THE TRIETHYL FRACTION

NO.	MOLES C_2H_4		BENZENE	MONO-	DI-	TRI-	TETRA-	PENTA-	HEXA-	SYM.
1	1.03	E		27	24	12	8	11	18	
		T	50	27	12	3	1	2	3	4
		B	16	14	8	15	10	3	7	75
2	2.14	E		9	45	28	13	2	3	
		T	2	19	51	18	8	1	1	61
		B	—	25	26	42	1	1	5	95
3	3.17	E		0.3	9	56	25	4	6	
		T	—	1	15	60	20	2	2	58
		B	—	—	—	57	21	7	15	70
4	4.22	E		—	1	17	37	27	18	
		T	—	—	1	24	41	22	12	56
		B	—	—	—	—	28	45	27	—
5	5.29	E		—	—	—	11	39	50	
		T	—	—	—	—	15	43	42	—
		B	—	—	—	—	4	29	67	—

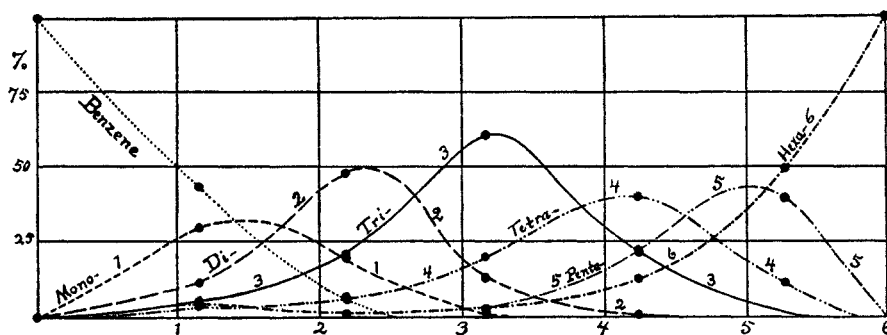


FIG. 1. MOLES OF ETHYLENE INTRODUCED. MOLE PERCENTAGES OF ETHYLATION PRODUCTS PRESENT AT DIFFERENT STAGES OF ETHYLATION

previously. It actually decreases during the introduction of the second and third moles of ethylene.

Benzene-aluminum chloride ratio. There has been a wide variation in the

benzene-aluminum chloride ratio in ethylation experiments by various authors. Balsohn (1) used 14:1, while 1.4:1 has been recommended for the preparation of 1,3,5-triethylbenzene (2). In Table II are the results of runs in which this ratio was varied from 4 moles of benzene to 1 of aluminum chloride to 23:1, 3 moles of ethylene being added in each. The runs in which this ratio is less than 10 show little difference. More aluminum chloride produces more triethyl- with a higher percentage of the 1,3,5-isomer and less of the di- and penta-ethyl.

Temperature effect. In Table III are data for two runs at a temperature lower than usual and for two at a higher. Since the reaction does not start well at

TABLE II
EFFECTS OF VARYING THE BENZENE-ALUMINUM CHLORIDE RATIO. DISTRIBUTION OF 3
MOLES OF ETHYLENE AND THE COMPOSITIONS OF THE TOP AND BOTTOM LAYERS.
ALSO THE PERCENTAGE OF THE 1,3,5-ISOMER IN THE TRIETHYL FRACTION

NO.	C ₆ H ₆ /AlCl ₃		BENZENE	MONO-	DI-	TRI-	TETRA-	PENTA-	HEXA-	SYM.
6	4	E		0.1	5	60	30	1.4	3.5	
		T	0.4	0.6	10	63	24	1	1	65
		B	—	—	1	64	29	1	5	75
7	6.3	E		0.1	5	63	27	1	3.8	
		T	0.6	0.4	9	67	22	1	0.4	62
		B	—	—	5	67	20	1	7	77
8	9	E		0.1	6	60	28	2.5	3.2	
		T	0.8	0.5	11	65	22	1	0.2	58
		B	—	—	1	56	24	5	14	71
9	18	E		0.2	9	52	29	4	6	
		T	0.3	0.8	16	56	23	2	2	48
		B	—	—	—	50	24	9	17	67
10	20	E		0.4	10	51	27	6	5	
		T	0.5	1.5	17	54	21	4	2	48
		B	—	—	—	53	25	8	13	—
11	23	E		0.2	9	45	28	12	5	
		T	0.3	0.9	17	50	22	8	2	48
		B	—	—	—	43	23	10	14	—

the lower temperature and since benzene boils below the higher, all of these were started as usual and the temperatures adjusted as soon as circumstances would permit. The distribution of the ethylene is shown in Figs. 2 and 3. The results at 95° are much like those at 75°, the usual temperature, but those at 55° are markedly different, there being less tri- and much more hexaethyl.

The effect of water. A small amount of water has a remarkable accelerating effect on the absorption of ethylene in the early stages of the reaction as is shown in Fig. 4. With 0.2% the rate starts to fall off at 1.5 mole, with 0.5% at 1.1 and with 1% at 0.9 mole while with 2% the absorption starts well but soon ceases

TABLE III
EFFECT OF TEMPERATURE. DISTRIBUTION OF THE ETHYLENE AND THE COMPOSITIONS
OF THE TOP AND BOTTOM LAYERS

NO.	TEMP., °C	MOLES C ₂ H ₄		BENZENE	MONO-	DI-	TRI-	TETRA-	PENTA-	HEXA-	SYM.
12	55	2.09	E		9	28	27	9	11	16	
			T	21	20	30	15	5	5	4	15
			B	—	11	25	44	1	6	13	64
13	95	2.17	E		8	45	41	3	0.3	3	
			T	2	17	51	28	2	0.1	0	65
			B	—	16	33	39	0.3	0.4	11	90
14	55	3.03	E		2	17	31	12	14	24	
			T	8	8	30	27	10	7	10	15
			B	—	1	7	50	1	16	25	59
15	95	3.22	E		0.1	6	59	28	3	4	
			T	0.1	0.4	11	64	23	1	0.5	62
			B	—	—	—	55	17	7	20	62

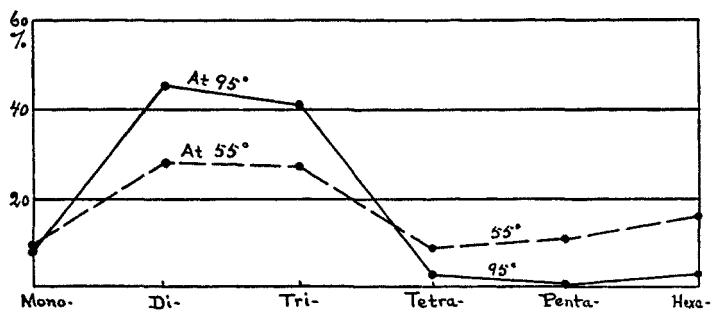


FIG. 2. TEMPERATURE EFFECT. PERCENTAGE DISTRIBUTION OF ETHYLENE WHEN TWO MOLES ARE INTRODUCED AT TWO DIFFERENT TEMPERATURES

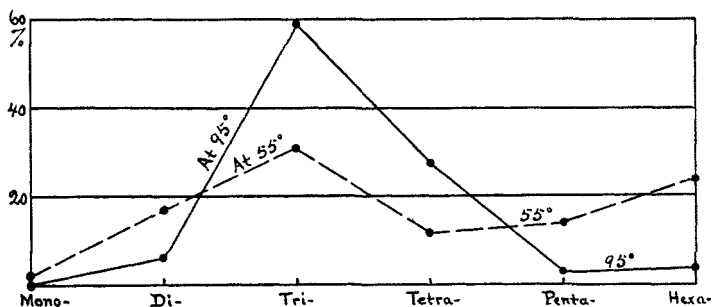


FIG. 3. TEMPERATURE EFFECT. PERCENTAGE DISTRIBUTION OF ETHYLENE WHEN THREE MOLES ARE INTRODUCED AT TWO DIFFERENT TEMPERATURES

entirely. The ethylene was admitted as fast as it was absorbed instead of at the usual constant rate. Runs had to be made changing other conditions to

get at the reason for the abnormal results of Runs 18 and 19 which showed large amounts of hexa- and small amounts of tri-ethyl. The results are in Table IV and some are plotted in Fig. 5. With reference to the distribution of the ethylene these two-mole runs fall into two classes, the normal in which over 40% of the ethylene appears in the diethyl and only 2-4% in the hexaethyl and those in which about 20% is in the di- and 37-50% in the hexa-ethyl.

Speed of ethylation. A run was made with the benzene-aluminum chloride ratio 6.3 and stirring at 12,000 r.p.m. After 1.7 moles of ethylene had been added, the absorption was at the rate of 1622 cc., or 0.07 mole, per minute per mole of benzene, or 18 volumes to one of the original benzene. This is double the rate previously attained, and about 20 times the rate used by Smith and Guss with ethyl chloride (3).

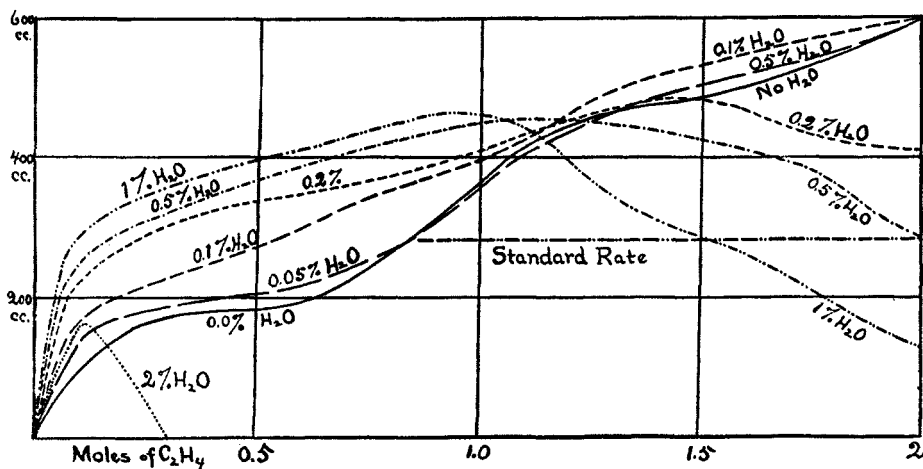


FIG. 4. EFFECT OF WATER. RATES OF ABSORPTION OF ETHYLENE IN THE PRESENCE OF DIFFERENT AMOUNTS OF WATER

Discussion of results. Taken as a whole, the results give strong support to the view that a part of the benzene is alkylated completely, and that then the hexaethyl is broken down largely to 1,3,5-triethylbenzene. If the ethylene is introduced at a moderate rate the tearing down of the highly alkylated products may keep pace with their building up and the results will be such as are represented in Fig. 1. It is possible that the proportions there shown would have been altered somewhat if the stirring and heating had been prolonged after all of the ethylene was in. When the amount of catalyst is small, the temperature low, or the ethylene is crowded in, the redistribution lags behind; more of the hexa- remains and less of the 1,3,5-triethyl is formed. When the conditions of the ethylation are considered this seems reasonable. The ethylation is concentrated on the hydrocarbons that are present in the heavy catalytic layer. If the amount of this is small or if diffusion between it and the top layer is poor the ethylene will not be distributed.

TABLE IV
EFFECTS OF WATER AND OF OTHER VARIABLES. DISTRIBUTION OF THE ETHYLENE AND THE
COMPOSITIONS OF THE TOP AND BOTTOM LAYERS

NO.	WATER	$\text{C}_2\text{H}_4/\text{AlCl}_3$	RATE	C_2H_4 MOLES		BEN- ZENE	MONO-	DI-	TRI-	TETRA-	PENTA-	HEXA-	SYM.
16	0.0	13	a	2.23	E		8	44	35	7	2	4	
					T	1	18	51	24	4	1	1	47
					B	—	10	29	47	1	3	10	70
17	0.05	13	a	2.15	E		9	44	36	5	2	4	
					T	2	20	49	24	3	1	1	52
					B	—	11	31	44	1	5	8	84
18	0.10	13	a	2.16	E		11	22	19	8	3	37	
					T	19	26	23	13	5	1	13	5
					B	—	12	37	24	1	4	22	72
19	0.20	13	a	2.36	E		11	19	14	11	3	42	
					T	15	27	22	11	7	1	17	3
					B	—	15	30	20	1	9	25	82
20	0.50	13	a	2.50	E		10	22	19	11	1	37	
					T	9	27	27	14	7	1	15	6
					B	—	13	33	34	1	2	17	77
21	0.20	13	1 ^c	2.20	E		8	44	38	4	3	3	
					T	1	17	52	26	2	1	1	52
					B	12	13	23	43	2	1	6	85
22	0.0	13	2.1	2.52	E		10	19	15	4	2	50	
					T	14	25	24	12	3	1	21	3
					B	—	19	31	23	—	9	18	78
23	0.0	6.3	2.1	2.21	E		7	45	44	1	1	2	
					T	1	15	51	30	1	1	1	60
					B	—	13	30	48	1	2	6	75
24 ^b	0.0	13	2.1	2.17	E		8	44	39	4	2	3	
					T	2	17	50	27	2	1	1	54
					B	6	18	23	43	2	1	7	79

^a The ethylene was added as fast as it was taken up.

^b The stirring was raised to 12,000 r.p.m.

^c 1 = 268 cc. per mole per minute.

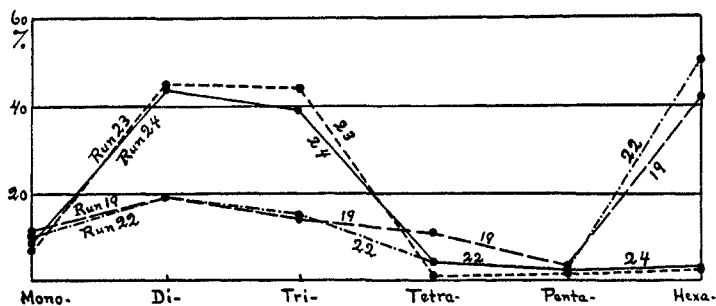


FIG. 5. DISTRIBUTION OF ETHYLENE WHEN TWO MOLES ARE INTRODUCED UNDER DIFFERENT
CONDITIONS

The remarkably high hexa- and low 1,3,5-triethyl- found in Runs 18, 19, and 20 were at first attributed to the influence of the water but the normal results of Run 21 with water present indicate that the cause was rather the crowding in of the ethylene. In Run 22 the initial ethylene absorption was speeded up with hydrogen chloride, and results obtained similar to those of Run 19. The high rate of ethylene introduction was taken care of in Run 23 by doubling the amount of aluminum chloride and in Run 24 by increasing the rate of stirring. The distribution of the ethylene is dependent on the diffusion between the two layers and the diffusion, in turn, is proportional to the area of

TABLE V

THE MOLE PERCENTAGES OF HEXA-, 1,3,5-TRI-, AND 1,2,4-TRIETHYL. ALSO r , THE RATIO OF THE CONCENTRATION OF THE 1,3,5-TRIETHYL IN THE BOTTOM LAYER TO THAT IN THE TOP

NO. RUN	HEXA-	1,3,5-	1,2,4-	r
Two moles of ethylene				
23	0.9	20	12	2.0
24	1.2	16	12	2.3
21	1.2	15	13	2.7
17	1.2	14	12	3.0
16	1.4	13	13	2.9
18	13	1.5	12	26
20	15	2.0	14	31
19	18	1.2	10	50
22	21	1.2	12	50
Three moles of ethylene				
8	1.7	38	26	1.1
6	1.9	44	21	1.1
7	2.0	43	23	1.3
15	2.0	39	24	0.9
10	2.4	27	27	1.4
11	2.8	25	25	1.2
3	3.0	35	24	1.1
9	3.0	28	28	1.3
14	12.2	7	24	7.4

the interface. Breaking the catalytic layer up into smaller droplets has the same effect as increasing its amount.

In Table V the results of two-mole runs are grouped together, arranged according to the amounts of hexaethyl present. In each run the triethyl is divided into its symmetrical and unsymmetrical parts and the ratio of these in the two layers is shown. The same is done for the three-mole runs. During the addition of the third mole of ethylene there is opportunity for the redistribution of the alkyls in the products already formed. Hence these runs should not differ as much as those with two. This is found to be true.

The total amount of the triethyl decreases from top to bottom in each part of the table but the amount of the unsymmetrical is markedly constant, regardless of the conditions. With 2 moles of ethylene the unsymmetrical is between 10% and 13% while the 1,3,5-isomer varies from 1.2% to 20%. Under conditions which do not favor redistribution, the symmetrical is relatively scarce and is concentrated in the bottom layer. With 3 moles of ethylene the results are similar but not so striking.

A high yield of 1,3,5-triethylbenzene may be obtained by passing in 3 moles of ethylene with even a low amount of aluminum chloride provided the temperature is high or the agitation vigorous. A triethyl fraction containing better than 95% of the unsymmetrical isomer may be obtained by taking the top layer of a low-temperature run in which the ethylene absorption rate is kept at the maximum.

SUMMARY

1. It has been found that the conditions of the ethylation of benzene, temperature, rate of introduction of ethylene, speed of stirring, and amount of aluminum chloride catalyst, greatly influence the proportions of the products.

2. These effects have been studied so as to throw light on the mechanism of the reaction.

3. The results appear to show that a part of the benzene is carried to the hexaethyl and that this is then dealkylated to a sort of equilibrium mixture containing much of the symmetrical triethylbenzene.

BALTIMORE, MD.

REFERENCES

- (1) BALSOHN, *Bull. soc. chim.*, **31**, 531 (1879).
- (2) GATTERMAN, FRITZ, AND BICK, *Ber.*, **32**, 1122 (1899).
- (3) SMITH AND GUSS, *J. Am. Chem. Soc.*, **62**, 2625 (1940).