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Aromatization of Ethylene and C4 Hydrocarbons Using a Thermal Diffusion Column

Yuzuru Takagi,* Toshiaki Aoyagi, Takeo Yoshida, Satoru Yada,
Tatsuaki Yamaguchi,[†] Yasuaki Esumi,[††] and Kazunori Tanaka[†††]
Department of Chemistry, College of Humanities and Sciences, Nihon University,
Setagaya, Tokyo 156
[†] Chiba Institute of Technology, Narashino, Chiba 275
[††] The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01
[†††] Department of Industrial Chemistry, Junior College of Engineering, Shizuoka University,
Johoku 3-5-1, Hamamatsu, Shizuoka 432

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Thermal diffusion columns, consisting of water-cooled glass tubes and a coaxial red-hot metal wire, were applied as the reactor to dehydrogenative coupling of ethylene or C_4 hydrocarbons. This application was intended to separate hydrogen spontaneously from other products, especially from aromatics, leading to enhanced yields. Hydrogen gas would ascend the red-hot wire, while the aromatics would descend the cold glass walls. When the metal wire was actually red-hot in the reactant hydrocarbon flow, oily products were really formed, most of which were mono- and bicyclic aromatic compounds such as benzene, styrene, and naphthalene. Product distributions were measured for different reactant species, wire metals, wire temperatures, and a few additional variables. Especially notable was the selective formation of 4-viny-1-cyclohexene from 1,3-butadiene at relatively low temperatures near 600 °C.

Recently, considerable interest has centered on activation of alkane C–H bonds, and a variety of attempts at such activation have been reported. Production of oily hydrocarbons from methane by Hirota[1–3] using thermal diffusion column as the reactor dates back to 1941, and ought to be regarded as one of the earliest examples of alkane activation. Regrettably however, this work has received little attention until very recently. In 1988, one of us (T. Y.)[4] re-examined Hirota's reaction process, confirming the conversion to oily products, and found that selective formation of C_2 hydrocarbons is also feasible under favorable reaction conditions.

Conversion of methane to higher hydrocarbons is always accompanied by hydrogen evolution. One advantage of using a thermal diffusion column as the reactor is that spontaneous separation of this hydrogen from higher hydrocarbon products is possible. This separation serves to enhance methane conversion by retarding otherwise unavoidable reverse reactions.

Hopefully, conversion of low hydrocarbons other than methane is also possible using a thermal diffusion column. In the present study, we employed ethylene as the main feed gas. For comparison, several C_4 hydrocarbons (butane, isobutane, 1-butene, isobutylene, 1,3-butadiene) were also examined as alternate feed gases.

Experimental

Apparatus. The flow-type reaction system used for aromatization is shown schematically in Fig. 1. Two different thermal diffusion columns, type L and type A, were designed as shown in Fig. 2, and used as reactors. Briefly, type L consists of a Pyrex-glass Liebig-type condenser (1 m in length and 2 cm in diameter) and a heatable metal wire mounted at the axis of the condenser tube. For type A, the Liebig-type condenser was replaced by Allihn type. The heatable metal wire in either type was renewable. Most reaction data were taken on a red-hot Nichrome wire of 70 cm length and 0.5 mm diameter, but other lengths down to 15 cm were also used. Besides Nichrome, three more materials were also tested as the heatable wire, viz., W, Ni, and Moleculoy (75% Ni, 20% Cr, 3% Al, and 2% Co). Cooling water was supplied from a circulating thermostat.

Temperature of heated wires was measured by a radiation pyrometer, Minolta IR-630. Most of the reaction products were identified by a double focussing GC-MS (gas chromatograph-mass spectrometer), Hitachi GC-MS M-80. Glass GC columns used in this identification were a 3 or 4.4 m × 3 mm i.d. column of Gaskuro-pack 55 (Gasukuro Kogyo Inc.) for gaseous components, and a 2 m × 3 mm i.d. column of polyethylene glycol for liquid components. These columns were also employed for quantitation of each

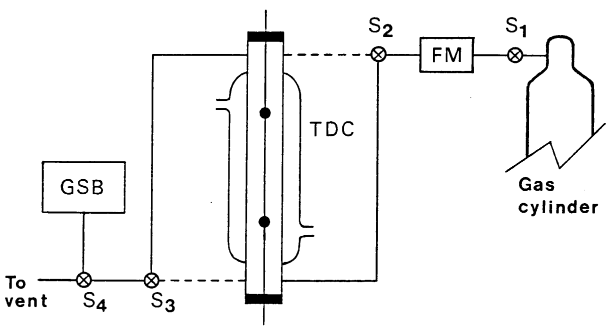

Fig. 1. Flow line for hydrocarbon aromatization using thermal diffusion column. FM, flowmeter; GSB, gas storage bag; S, stopcock; TDC, thermal diffusion column.

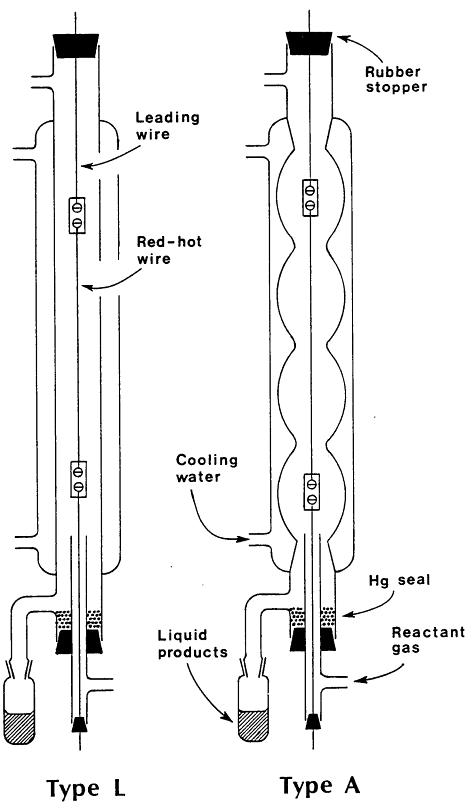

Fig. 2. Two types of thermal diffusion columns used as reactor.

component molecule by ordinary GC, which was done using a thermocouple detector for the gaseous products, and a flame ionization detector for the liquid products.

Procedures. Aromatization of ethylene and C_4 hydrocarbons was carried out using the flow line of Fig. 1 as follows. One of the hydrocarbons was fed from the gas cylinder into the line with stopcock S_4 open to the atmosphere. Unless otherwise stated, the feed was passed through the thermal diffusion column in the ascending direction by means of stopcocks S_2 and S_3. A certain time was allowed for air replacement with feed, then the metal wire was heated to the desired temperature, and maintained at that temperature for 2 h. About 15 min after wire heat-up, stopcock S_4 was switched to the storage bag to collect the gaseous products for a certain period of time, usually 1 h. The gaseous sample in the storage bag was separated and quantified by GC with reference to appropriate calibration curves constructed using authentic samples. Liquid products descending the water-cooled glass walls were collected into the bottom finger (Fig. 2) over the full duration of the 2-h wire heating.

Data Analysis

Product Yield. Both ethylene and C_4 hydrocarbon feeds were converted into a variety of other hydrocarbons (i.e., gaseous and liquid products) by passage through the thermal diffusion column. For data analysis, let us number these hydrocarbons from 1 to integer *i*, and let symbol *f* represent the reactant feed, with or without subscript $\circ$ which refers to the state of no conversion before passing through the thermal diffusion column. Percentage molar conversion, Y_i, of the feed to the *i*-th product molecule, with respect to carbon balance, may be defined as

$$Y_i = 100 n_i M_i / n_f M_{f_\circ} \tag{1}$$

where $M_{f_\circ}$ is the number of moles of the reactant feed supplied over a certain period of time, n_f is the carbon number of the feed molecule, M_i is the number of moles of the *i*-th product molecule formed, and n_i is its carbon number, The quantity $M_{f_\circ}$ is given as the product of the reaction time or feeding duration and the flow rate monitored by flowmeter FM (Fig. 1). To estimate M_i for gaseous products from the GC data, their peak areas were calibrated using reference gas samples (propylene and 1-butene for unidentified C_3 and C_4 peaks, respectively).

In the case of liquid samples, owing to the use of flame ionization detector, their GC peak areas are roughly proportional to the carbon content of the sample. Consequently, we have an approximate relationship such as:

$$n_{i(l)} M_{i(l)} = k A_{i(l)} \tag{2}$$

where subscript (l) refers to the liquid state, $A_{i(l)}$ is the GC peak area of the *i*-th liquid component , and *k* is the proportionality constant common to all *i* components. Thus, Eq. 2 allows for evaluation of relative $n_{i(l)} M_{i(l)}$ values for all liquid components, even if their GC peaks are unidentified.

Sometimes major interest focusses on either liquid or gaseous products alone. For liquid products in particular, it is convenient to apply Eq. 1 only to the liquid components and summate them:

$$\sum_i Y_{i(l)} = 100 \sum_i n_{i(l)} M_{i(l)} / n_f M_{f_\circ} \tag{3}$$

This summation, $\sum_i Y_{i(l)}$, is the percentage molar conversion of the feed to those liquid products collected in the bottom finger of the thermal diffusion reactor. For the gaseous sample collected in the gas storage bag, on the other hand, we have

$$\sum_i Y_{i(g)} = 100 \sum_i n_{i(g)} M_{i(g)} / n_f M_{f_\circ} \tag{4}$$

where subscript (g) refers to the gaseous state. The summation $\sum_i Y_{i(g)}$ is the precentage molar conversion of the feed to other gaseous components. Similarly, for the unreacted part of the reactant feed

$$Y_f = 100 M_f / M_{f_\circ} \tag{5}$$

where M_f is the number of moles of the unreacted feed, and hence Y_f is the percentage of the unreacted part in the reactant feed.

Product Distribution. For the liquid sample collected in the bottom finger, we can define its consitituent composition or product distribution by:

$$Z_{i(l)} = 100\, Y_{i(l)} / \sum_i Y_{i(l)} = 100 n_{i(l)} M_{i(l)} / \sum_i n_{i(l)} M_{i(l)} \qquad (6)$$

It should be noted that the composition defined by $Z_{i(l)}$ is carbon-number weighted. For the gaseous product sample collected in the storage bag, we have a similar expression:

$$Z_{i(g)} = 100\, Y_{i(g)} / \sum_i Y_{i(g)} = 100 n_{i(g)} M_{i(g)} / \sum_i n_{i(g)} M_{i(g)} \qquad (7)$$

Although produced hydrogen and unreacted feed olefin are also collected in the gas storage bag, they are not included in Eq. 7. Taking unreacted olefin into account we have, instead of Eq. 7:

$$Z_{if(g)} = \frac{100 n_{i(g)} M_{i(g)}}{\sum_i n_{i(g)} M_{i(g)} + n_f M_f} \qquad (8)$$

for product hydrocarbons, and

$$Z_{ff(g)} = \frac{100 n_f M_f}{\sum_i n_{i(g)} M_{i(g)} + n_f M_f} \qquad (9)$$

for unreacted feed. These quantities $Z_{if(g)}$ and $Z_{ff(g)}$ may be interpreted as representing "the carbon-number weighted molar percentage composition" for carbonaceous gaseous samples collected in the gas storage bag.

Results and Discussion

Preliminary Tests. Choice of the reactor type used (L or A) did not significantly affect liquid product yield, $\sum_i Y_{i(l)}$, nor liquid product composition, $Z_{i(l)}$. Thus, our kinetic data will be given without specifying reactor type used. In order to determine the appropriate length of the red-hot wire (Nichrome) in the reactor, its length was varied in a range of 15—70 cm, and the value of $\sum_i Y_{i(l)}$ was measured using ethylene as the feed (wire temperature ca. 890 °C, flow rate $57 \pm 3\ \mathrm{cm^3\ min^{-1}}$). Liquid product yield, $\sum_i Y_{i(l)}$, increased with increasing wire length in the low region of 15—40 cm, but beyond 40 cm it was almost constant. Product distributions, expresed in terms of $Z_{i(l)}$, were also nearly identical within the 40—70 cm region. Thus, we employed 50- and 70-cm long wires in most experiments.

Repeated use of the metal wire in the thermal diffusion reactor, i.e., repeated red-hot heating in the hydrocarbon feed, probably caused carbonaceous deposition on the wire. This was judged from its appearance and also from methane formation observed when the spent metal wire was red-hot heated in a H_2 stream. However, we

Table 1. Aromatization of Ethylene over Nichrome Wire

Run No.		1	2	3	4	5	6	7	8
Reaction conditions	Nichrome wire temp/°C	780	850	890	950	810	810	810	810
	Glass wall temp/°C	20	20	20	20	5	20	35	50
	Nichrome wire length/cm	70	70	70	70	15	15	15	15
	Electric power/watt	300	310	390	470	79	84	85	81
	Flow rate/$\mathrm{cm^3\ min^{-1}}$	60	60	60	60	9	9	9	9
Total yield of liquid products $\sum_i Y_{i(l)}$/%		1.6	24.2	50.5	77.5	22.9	20.1	18.4	10.0
C-number weighted composition of liquid products: $Z_{i(l)}$/%		(Monocyclic)							
	Benzene	16.8	16.9	19.5	18.7	30.1	18.5	11.3	10.6
	Toluene	7.8	4.5	3.6	2.6	2.9	5.0	3.0	0
	Styrene	24.7	20.3	17.9	12.0	19.6	21.4	17.2	11.2
	Phenylacetylene	3.3	3.2	3.8	4.4	2.8	3.1	3.0	2.3
	m-Methylstyrene	1.1	0.5	0.3	0.1	0	0	0	0
	3-Phenyl-1-propene	3.1	1.0	0.5	0.2	0	0	0	0
		(Bicyclic)							
	Naphthalene	5.3	13.0	16.2	21.4	3.6	8.0	19.2	22.4
	Indene	9.7	10.7	10.8	9.2	3.1	11.8	11.4	9.6
	Biphenyl	1.0	2.2	2.8	3.5	0	0	0	0
		(Tricyclic and unidentified)							
	Acenaphthylene	0.5	1.3	2.5	4.7	0	0	0	0
	Unidentified	26.7	26.4	22.1	23.2	26.8	31.2	34.3	38.1
C-number weighted composition of gaseous components: $Z_{if(g)}$/% $Z_{ff(g)}$/%	CH_4	2.0		15.7					
	CH_2=CH_2 (Unreacted)	86.2		69.0					
	CH≡CH	0.4		4.0					
	CH_3–CH_3	1.4		1.0					
	C_3 components	7.4		10.3					
	C_4 components	2.6		0					

confirmed that, whether the metal wire was fresh or repeatedly used, almost identical kinetic data were obtainable under otherwise identical conditions. The metal wire was therefore repeatedly used over several runs without renewal.

Ethylene Aromatization. The effects of metal wire temperature upon the liquid product yield ($\sum_i Y_{i(l)}$) and the liquid product distribution ($Z_{i(l)}$) were studied with a Nichrome wire, and the results are given in Table 1.[5] It is seen from Runs 1—4 that $\sum_i Y_{i(l)}$ dramatically increased from a very low value of 1.6% at 780 °C to a high value of 77.5% at 950 °C. In contrast, the temperature effect on $Z_{i(l)}$ was rather modest. The contents of naphthalene, biphenyl, and acenaphthylene increased with increasing wire temperature, whereas the proportions of most monocyclic compounds, with the exception of benzene and phenylacetylene, decreased. Enrichment of bicyclic compounds at the expense of monocyclic compounds was also seen as the glass wall temperature (i.e., cooling water temperature) was raised (Runs 5—8). Presumably, the red-hot wire functions as a "producer" of various radicals, and their reactions, such as addition and oligomerization, occur on or near the glass walls. The higher the wall temperature, the greater the likelihood that radical reactions would be promoted, allowing for production of polycyclic compounds, rather than monocyclic ones.

Of further interest is the formation of odd carbon-number compounds such as toluene and indene. This is consistent with the appearance of methane in the gaseous mixture, as confirmed in Runs 1 and 3 (Table 1). Although direct hydrocracking of ethylene or other C_2 hydrocarbons is not deniable, it is more likely that methane is formed mainly by the C–C bond cleavage of cycloparaffin or cycloolefin intermediates such as methylcycloheptane, 1,5-cyclooctadiene, and 4-vinyl-1-cyclohexene (4V1C)[6,7]

Figure 3 shows the effects of the flow rate and flow direction of ethylene upon the total yield, $\sum_i Y_{i(l)}$, of the

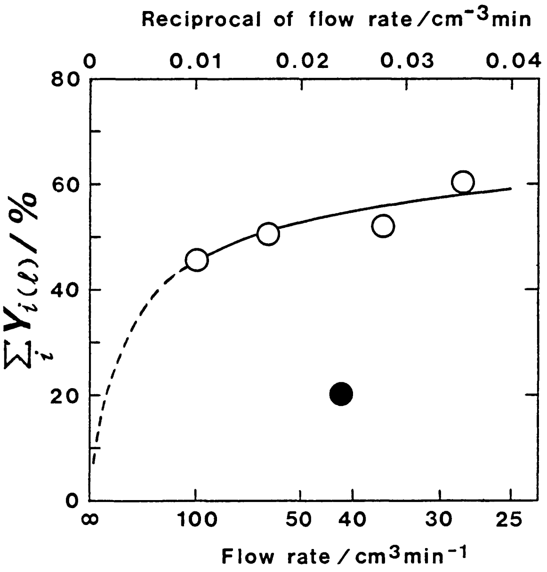

Fig. 3. Effects of flow rate and flow direction of ethylene upon total yield of the liquid products. Open circles, for ascending flow in the thermal diffusion column; closed circle, for descending flow in the thermal diffusion column. The reaction conditions used for these experiments were quite similar to those of Run 3 (Table 1) except for flow rate.

Table 2. Aromatization of Ethylene over Various Metal Wires

Run No.		61	62	63	64
Reaction Conditions	Heatable wire	Nichrome	W	Ni	Moleculoy
	Wire o. d./cm	0.05	0.02	0.05	0.02
	Electric power/watt	260	230	290	950
		(Common to all runs)			
	Wire temperature/°C	830±10			
	Flow rate/cm^3 min^{-1}	55±3			
	Wire length/cm	50			
Total yield of liquid products $\sum_i Y_{i(l)}$/%		7.7	32.6	14.6	41.1
		(Monocyclic)			
C-number weighted composition of liquid products: $Z_{i(l)}$/%	Benzene	11.8	19.0	16.3	23.2
	Toluene	4.6	4.9	5.0	5.0
	Styrene	20.1	21.9	24.0	20.3
	Phenylacetylene	3.5	4.6	3.7	4.9
	m-Methylstyrene	0.8	0.4	0.6	0.3
	3-Phenyl-1-propene	2.0	0.8	1.4	0.7
		(Bicyclic)			
	Naphthalene	10.8	11.2	12.0	11.5
	Indene	13.2	12.2	12.7	13.4
	Biphenyl	2.0	1.8	1.7	1.8
		(Tricyclic and unidentified)			
	Acenaphthylene	1.1	1.6	1.3	1.8
	Unidentified	30.1	21.6	21.3	17.1

Table 3. Aromatization of C_4 Hydrocarbons

	Run No.	41	48	40	39	37	54	49	59	43
	Reactant gas	1,3-Butadiene					Butane	Isobutane	1-Butene	Isobutylene
Reaction conditions	Nichrome wire temp/°C	620	620	690	750	830	830	810	810	810
	Flow rate/cm^3 min^{-1}	53	29	53	53	53	32	52	32	62
	Wall temperature/°C	15	13	18	19	20	15	13	15	17
		(Commom to all the runs)								
	Wire length/cm					70				
Total yield of liquid products $\sum_i Y_{i(1)}$/%		2.9	16.8	18.5	43.4	69.3	23.3	10.2	39.2	28.2
C-number weighted composition of liquid products: $Z_{i(1)}$/%		(Monocyclic)								
	Benzene	0.4	1.4	7.5	18.5	29.9	22.2	23.8	29.8	20.9
	Toluene	1.5	3.7	10.9	15.8	9.6	6.6	11.4	9.3	16.9
	Styrene	0	0.1	0.6	2.9	10.3	20.8	15.1	12.2	3.9
	Phenylacetylene	0	0.2	1.8	1.8	0.2	3.8	3.9	2.5	1.6
	m-Methylstyrene	0	0	0.2	0.2	0.9	0.6	2.1	0.7	2.6
	3-Phenyl-1-propene	0	0	0.3	2.5	2.2	0.9	1.5	1.2	0.8
	4-Vinyl-1-cyclohexene (4V1C)	85.5	81.8	56.6	18.5	1.1	0	0	0	0
		(Bicyclic)								
	Naphthalene	0	0	0	0.3	5.4	9.3	5.4	4.8	1.8
	Indene	0	0.1	0.3	1.9	6.7	8.0	6.7	4.9	4.0
	Biphenyl	0	0	0	0	0	2.3	1.4	1.7	0.8
		(Tricyclic and unidentified)								
	Acenaphthylene	0	0	0	0	0	0.3	0.5	0.5	0.5
	Unidentified	2.9	16.8	18.5	43.4	69.3	24.5	28.2	32.4	46.4

liquid components. The four open circles represent the data for the ascending flow in the thermal diffusion column, and the curve passing through these data points indicates that $\sum_i Y_{i(\mathrm{l})}$ increases with decreasing flow rate. Reversal in the flow direction apparently gave rise to a much lower $\sum_i Y_{i(\mathrm{l})}$ value (closed circle), i.e., a poorer yield of aromatics. Product compositions ($Z_{i(\mathrm{l})}$) for these five runs differed little from one another, and were close to that of Run 3 (Table 1).

One might expect product selectivity, i.e., the composition of the liquid products $Z_{i(\mathrm{l})}$, to vary greatly depending on the material of the red-hot wire. This was examined by comparing four different materials as the wire, viz., Nichrome, tungsten, nickel, and Moleculoy. However, as shown in Table 2, the $Z_{i(\mathrm{l})}$ values were rather similar. Such similarity again suggests that the hot wire functions as a mere radical generator, and that the subsequent radical reactions leading to aromatics are catalyzed in regions remote from the red-hot wire.

C_4 Hydrocarbon Aromatization. Experimental results with C_4 hydrocarbon feeds are summarized in Table 3. Most noticeably, 1,3-butadiene is distinguished from other C_4 and ethylene feeds in that it produced 4V1C; especially at a temperature as low as 620 °C where it amounted to more than 80% of the liquid products ($Z_{i(\mathrm{l})}$). The $Z_{i(\mathrm{l})}$ value for 4V1C decreased with increasing wire temperature. Reports in the literature indicate that two 1,3-butadiene molecules can undergo the Diels–Alder [4 + 2] cycloaddition to form 4V1C.[8,9]

It is likely that the wire temperature of 620 °C is not high enough to produce radicals to a sigificant extent so that the cycloaddition of 1,3-butadiene itself prevails, leading to high selectivity toward 4V1C. With the progressive elevation of the wire temperature to 690 °C, 750 °C, and finally to 830 °C, however, more and more radicals may be produced on the red-hot wire, and at 830 °C radical reactions overwhelm the cycloaddition, reducing the $Z_{i(\mathrm{l})}$ value for 4V1C to a very low 1.1%.

Concluding Remarks. In general, the liquid product composition, $Z_{i(\mathrm{l})}$, is not very sensitive to wire material or wire temperature, nor to the hydrocarbon fed. However, it does seem to depend strongly on outer glass wall temperature. Elevating the wall temperature from 5 to 50 °C, raised the naphthalene composition remarkably at the expense of monocyclic constituents, such as benzene and styrene (Runs 5—8, Table 1). This effect of wall temperature merits further study. Since the wall is expected to function as a catalyst for radical cyclization and related reactions, it is also of interest to examine possible variations of the product composition, $Z_{i(\mathrm{l})}$, when wall materials other than glass are used.

As yet we do not have sufficient data to discuss the reaction mechanism produced in the thermal diffusion column. However, it is tempting to speculate that C_2 radicals tetramerize and C_4 radicals dimerize, both forming octene- or cyclooctadiene-type intermediates which in the subsequent reactions are converted to aromatics such as benzene, toluene, and styrene.[6,7,10] Naphthalene might possibly be produced by the reaction of toluene and C_3 species as well as styrene and C_2 species.

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References

1) K. Hirota, *Bull. Chem. Soc. Jpn.,* **16**, 274 (1941).

2) K. Hirota and K. Oguro, *Nippon Kagaku Kaishi,* **64**, 1097 (1943).

3) K. Hirota and K. Oguro, *Nippon Kagaku Kaishi,* **64**, 1178 (1943).

4) T. Yamaguchi and C. Saito, *Bull. Chem. Soc. Jpn.,* **61**, 2469 (1988).

5) In respnse to the referee's comment on material balance, we performed an additional experiment to estimate values for $\sum_i Y_{i(\mathrm{g})}$ and Y_f under identical conditions with those for Run 3, Table 1. They were 11.1 and 29.1%, respectively. These values and the corresponding total yield of liquid products ($\sum_i Y_{i(\mathrm{l})}$), 50.5%, add up to 90.7% — a relatively good carbon balance with ethylene feed.

6) R. Maurel and J.-E. Germain, *Bull. Soc. Chim. Fr.,* **1960**, 930.

7) C. T. Goetschel and H. Pines, *J. Org. Chem.,* **30**, 3544 (1965).

8) K. Ziegler and H. Wilms, *Justus Liebigs Ann. Chem.,* **567**, 1 (1950).

9) J. C. Hillyer and J. V. Smith, Jr., Ind. Eng. Chem., **45**, 1133 (1953).

10) a) N. D. Zelinsky and M. B. Turowa-Pollak, *Ber.,* **56**, 1171 (1923); b) H. S. Taylor and J. Turkevich, *Trans. Faraday Soc.,***35**, 921 (1939); c) E. F. G. Herington and E. K. Rideal, *Proc. R. Soc. London, Ser. A,* **184**, 434 (1945); d) H. Pines, E. F. Jenkins, and V. N. Ipatieff, *J. Am. Chem. Soc.,* **75**, 6226 (1953).
