The situation is similar to that of the pyridones, where zwitterionic forms contribute significant stabilization to the ground state of the molecule.[2] According to Elvidge and Jackman,[17] 2-pyridone possesses only ~35% the aromaticity of benzene, receiving 10–15 kcal. of stabilization from the zwitterionic forms.

In many respects, the naphthalene Schiff bases can be considered γ-pyridones, with the polar forms contributing stabilization to the system, but not being the predominant one in solution.[18] If the structure of the naphthalene Schiff base is assumed to consist of 30–50% of the polar forms **7**, then the 20–24 kcal. of resonance energy lost in de-aromatizing one ring of the naphthalene system will be reduced to 10–15 kcal.

The observation of spin–spin coupling of the amine proton to the adjacent methylene is excellent evidence for the presence of the keto-amine form. Unfortunately, the absence of an observable coupling is not absolute evidence for the presence of the phenol-imine form. As the energy barrier to the tautomeric interconversion of a proton between nitrogen and oxygen decreases, exchange between sites of the proton will become more rapid irrespective of the time spent in a given site—the exchange will eliminate the spin–spin coupling between the methylene and the acidic proton. For example, with acidified ethanol, the hydroxyl protons are located on oxygen but, owing to rapid exchange between sites, no coupling is observed. When the methylene protons adjacent to the nitrogen display no evidence of spin-coupling, more information is required to eliminate the possibility of rapid proton exchange between sites.

The existence of a large long-range spin–spin coupling in many of the supposed naphthol-imines with $J \approx$ 0.7–1.4 c.p.s. may be another useful criterion of an imine structure. According to Karplus,[19] long-range couplings found in unsaturated proton systems are due to the π-electrons of the double bond, the σ-system being insufficient to account for the values observed.

For example, the coupling of 0.8 c.p.s. observed in the 2,3- and the 2,6-naphthalene Schiff bases may imply the presence of a large amount of π-electron structure in the double bond, especially since values of 0.8 c.p.s. are found in the compounds formed by condensing benzylamine with acetophenone and 2-acetonaphthone. From resonance and chemical considerations, these compounds are expected to be phenol-imines. In order to form the keto-amine tautomer, both rings of the naphthalene must be quinoid—involving the loss of resonance energy in excess of 50 kcal. Even with some stabilization of the keto-amine tautomer by polar forms (similar to **7**), the net energy loss in forming the amine in these systems would be prohibitive. As an example of this situation, both the 1,2- and the 1,4-naphthoquinones are known compounds, while the 2,3- and the 2,6-naphthoquinones have yet to be synthesized.[20] Therefore the coupling arguments are quite consistent with what is expected from the chemistry.

The large coupling observed in one of the rotamers of N-methyl-2-hydroxy-1-acetonaphthone-imine likewise may be explained in a manner consistent with the long-range couplings. In chloroform solution, the singlets from the two methyls may be results of rapid exchange of the acidic proton between sites, while in pyridine solution, the unsplit methyl signals may be from the rotamer which is rapidly exchanging. The methyls split into quartets are from the rotamer without the hydrogen bond. The analysis of the shifts of the hydrogen at the 8-position of the ring is in agreement with this assumption.[18]

Acknowledgment.—I wish to thank Dr. Richard H. Holm and Dr. J. D. Baldeschwieler for several friendly discussions.

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Catalytic Cracking of Hydrocarbons. III. Product Distribution Obtained in Cracking Cetane over a Silica Alumina Catalyst at 372°

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Greensfelder's carbonium ion theory is applied with a few modifications to the catalytic cracking of hexadecane at 372°. Temperature is introduced into the calculation by use of the Boltzmann distribution and the estimated energies of formation of gaseous carbonium ions. Tracer results are employed to estimate the fraction of the initial olefin products undergoing further decomposition, alkylation and polymerization. Product distributions as a function of carbon number are calculated at 372 and 500°.

Introduction

An examination of the product distribution as a function of carbon number for some integral reactor tracer experiments[2] in cracking hexadecane at 372° over a silica–alumina catalyst reveals some major differences in comparison with the earlier results of Greensfelder at 500°.[3] The most striking of these differences is that found for C_4 hydrocarbons. Approximately 160 moles of C_4 per 100 moles of hexadecane cracked was observed at 372° compared with about 100 moles per 100 moles of hexadecane at the higher temperature. It is at once evident that a straightforward application of the type of calculation used by Greensfelder will not suffice to explain our distribution since this calculation is not at all temperature dependent. In the present paper we shall describe how we have modified Greensfelder's method of calculation by the inclusion of a temperature dependence based on values for the energies of formation of gaseous carbonium ions proposed by him,[4] and by making new estimates of the extent of secondary cracking of olefins based on our tracer experiments (see paper I of this series). The modified method accounts to a good approximation

(1) Abstracted in part from the Doctoral Thesis of W. A. Van Hook.

(2) See Paper I, this series, *J. Am. Chem. Soc.*, **84**, 4410 (1962).

(3) B. S. Greensfelder, H. H. Voge and G. M. Good, *Ind. Eng. Chem.*, **41**, 2573 (1949).

(4) B. S. Greensfelder, "The Chemistry of the Petroleum Hydrocarbons," Vol. II, edited by B. T. Brooks, *et al.*, Reinhold Publishing Corp., New York, N. Y., 1955, Chapter 27.

TABLE I

PRODUCTS OF REACTION IN MOLES FORMED PER 100 MOLES OF $C_{16}H_{34}$ CRACKED OVER A SILICA-ALUMINA CATALYST AT 372°

Peak no.	Product	Run I	II	III	IV	V
1	Methane	0.5	0.6	1.0	0.7	0.9
2	Ethylene	2.4	3.1	1.7	3.0	2.3
3	Ethane	1.8	2.7	1.3	2.2	1.7
4	Propane	33.2	43.1	37.7	35.6	36.9
5	Propylene	53.7	68.2	53.1	52.0	52.3
6	Isobutane	79.3	92.7	84.2	87.8	101.5
7	Isobutylene + 1-butene	28.1	29.1	27.8	30.5	34.7
8	*n*-Butane	13.4	13.7	16.5	13.3	17.3
9	*trans*-Butene-2	12.7	10.3	11.1	12.4	13.4
10	*cis*-Butene-2	7.8	6.2	7.0	9.0	9.6
11	Amylene (A)	6.2	7.5	5.6	6.3	2.9
12	Isopentane	40.2	33.5	38.8	34.3	41.0
13	1-Pentene	8.3	6.2	8.7	4.2	6.6
14	*n*-Pentane	4.8	6.0	9.8	4.2	6.4
15	Amylene (B)	14.4	16.0	20.1	17.8	11.8
16	2-Methylpentane	10.2	10.0	9.9	10.5	6.4
17	3-Methylpentane	6.0	6.5	6.5	6.3	3.9
18	*n*-Hexane and 1-hexene	3.8	3.7	3.1	3.5	2.4
19	2,4-Dimethylpentane	5.1	3.9	5.8	2.9	2.9
21	Isomeric heptane	3.5	3.0	2.9	2.8	2.0
22	Isomeric heptane	1.1	2.1	0.9	1.2	0.4
23	2-Methylhexane and 2,3-dimethylpentane	2.4	1.9	2.4	1.9	1.6
24	3-Methylhexane	2.5	2.3	2.9	2.5	1.8
26	*n*-Heptane and 1-heptene	1.6	1.1	1.7	1.2	1.2
27	Dimethylhexanes	1.4	0.8	1.1	1.0	0.7
28	Benzene	1.4	1.4	1.1	1.1	.8
29	Unresolved isomeric octanes	0.5	0.4	0.5	0.5	.4
30	Unresolved isomeric octanes	.1	.2	.1	.2	.4
31	Unresolved isomeric octanes	.7	.7	.8	.8	.5
32	Unresolved isomeric octanes	.8	.7	.8	.8	.6
33	*n*-Octane	.4	.5	.5	.6	.4
34	Unresolved isomeric nonanes	.2	.2	.1	.3	.1
35	Toluene	.8	.9	.9	.7	1.7
36	Unresolved isomeric nonanes	.4	.3	.3	.4	0.3
37	Unresolved isomeric nonanes	.3	.2	.2	.3	.2
38	*n*-Nonane	.1	.2	.1	.2	.2
39	Unresolved isomeric decanes	.1	.1	.1	.1	.1
40	*p*-Xylene and *m*-xylene	1.8	1.7	2.6	2.0	.9
41	*o*-Xylene	0.6	0.5	0.9	0.6	.6
42	*n*-Decane	.5	.2	.2	0.6	.2
43	*unsym*-Trimethylbenzene	.2	.5	.8	1.3	.6
44	*n*-Undecane	.9	1.2	1.3	2.9	1.0
45	Unresolved isomers of C_{12}, C_{13}	.6	0.5	0.6	1.5	0.6
46	Unresolved isomers of C_{12}, C_{13}	.5	.5	.5	1.0	.6
47	Unresolved isomers of C_{12}, C_{13}	.6	.6	.6	1.7	.4
48	*n*-Dodecane	.4	.3	.1	0.5	.7
	Total	356.3	386.0	374.7	365.2	373.9
	LHSV $C_{16}H_{34}$	0.54	0.42	0.41	0.44	0.36
	Conversion, %	26.2	34.4	31.9	34.3	37.5
	Estimated maximum time of contact (sec.)	11.4	11.7	11.7	11.6	11.9
	Feed (cc. gas/min.)					
	Helium	170	170	170	170	170
	$C_{16}H_{34}$	25.5	19.9	19.4	20.8	17.0
	Added tracer (* indicates radioactive tracers)	0.0	$0.3C_7H_{14}$	$0.3C_7H_{14}$	0.0	$0.01C_3H_6$*
	Duration of run (min.)	30	30	30	30	30
	Coke (wt. % of feed)	...	...	...	1.7	1.7
	Total mmoles cracked	8.86	9.06	8.21	9.44	7.51
	Carbon balance (blank indicates coke not detd.)	...	...	...	101.2	99.1

for the difference in composition of products at 372 as compared to 500°.

Experimental

The experimental apparatus and detailed procedure used for cracking hexadecane at 372° over a silica-alumina catalyst have been described in paper I of this series. It will suffice to point out that an integral reactor containing 37 cc. of cracking catalyst was used and the hexadecane at a feed rate of about 17 cc. of gas per minute was carried through the reactor with 170 cc. per minute of helium. The products were collected and analyzed by gas chromatography as described in the first paper.

Results

The product distributions from four control runs and six radioactive runs in the integral reactor are shown in Table I. Conversion of the data to moles of product for 100 moles of hexadecane cracked has been made

Run VI	VII	VIII	IX	X	Average	Average deviation
0.4	1.1	0.7	0.2	0.8	0.7	0.2
3.3	2.4	3.5	3.2	3.1	2.8	0.3
2.2	2.0	3.1	2.4	3.1	2.3	0.3
47.5	42.2	43.8	35.9	34.6	39.1	4.1
57.2	69.4	58.6	52.4	57.6	57.5	4.8
98.1	93.6	105.8	99.8	82.4	92.5	7.1
33.2	30.0	40.8	40.3	38.4	33.3	4.2
17.8	17.8	16.6	17.2	16.0	16.0	1.5
14.5	15.6	12.0	13.1	17.1	13.2	1.5
7.6	8.6	7.4	8.2	9.8	8.1	0.9
4.0	5.4	3.4	3.1	3.6	4.8	1.4
48.0	30.5	35.0	42.1	28.1	37.2	4.9
4.9	5.5	3.7	5.5	4.3	5.8	1.5
6.8	5.3	4.3	5.3	4.8	5.8	1.2
12.2	13.4	11.7	14.3	12.9	14.5	2.1
...	8.8	6.0	9.6	6.4	8.6	1.6
...	4.3	3.8	8.4	4.7	5.6	1.3
...	3.1	2.0	4.7	3.5	3.3	0.6
...	4.3	2.8	4.4	4.0	4.0	.8
...	3.0	1.8	3.0	2.9	2.8	.3
...	1.2	0.5	0.6	1.0	1.0	.3
...	2.0	1.3	1.6	1.3	1.8	.3
...	2.3	1.8	2.3	1.4	2.2	.3
...	1.5	0.9	1.3	3.8	1.3	.2
...	1.0	.7	0.9	1.1	1.0	.2
...	1.3	.6	1.0	0.6	1.0	.3
...	0.9	.4	1.4	.3	0.6	.3
...	.1	.1	0.1	.1	.2	.1
...	.6	.4	.5	.5	.6	.1
...	.7	.5	.6	.5	.7	.1
...	.5	.4	.6	.5	.5	.1
...	.1	.1	.2	.1	.2	.1
...	1.5	.9	.8	.7	1.0	.3
...	0.7	.7	.6	.3	0.4	.1
...	.4	.5	.5	.2	.3	.1
...	.3	.2	.3	.4	.2	.1
...	.1	.1	.1	.4	.1	.1
...	2.0	1.7	2.3	3.1	2.0	.4
...	0.4	0.6	0.8	0.6	0.6	.1
...	.2	.3	.3	0.4	.3	.1
...	.9	.5	.6	1.8	.8	.3
...	1.1	.4	1.2	1.7	1.3	.4
..	...	1.0	0.5	0.3	0.6	.2
...	0.3	0.8	.4	.3	.6	.2
...	.4	0.8	.4	.4	.7	.3
...	.5	1.1	.5	.2	.5	.2
...	387.3	384.1	393.5	360.1	$(\bar{\Sigma}) = 375.7 \pm 10.7$	$\Sigma i\,(\text{average})i = 378.4 \pm 36.6$
0.35	0.34	0.49	0.40	0.35		
35.6	24.1	39.3	35.0	34.4		
11.8	11.9	11.5	11.6	11.8		
170	170	170	170	170		
16.3	16.1	23.2	19.0	16.6		
$0.01C_3H_8$*	$0.01C_4H_{10}$*	$0.3C_7H_{14}$*	$0.3C_7H_{14}$*	$0.15C_7H_{16}$*		
8	40	30	30	40		
3.8	1.5	2.0	2.3	1.5		
3.08	6.62	11.54	8.67	10.0		
...	100.6	97.3	98.4	99.7		

from the observed amounts of product, percentage conversion, and the tabulated densities and molecular weights.

It is to be noted that for any one product agreement from run to run is about plus or minus 10% as judged by the average deviation, but for the sum of all products it is within about 3% by the same criterion. This tends to indicate that although slight changes in feed rates and other variables do change the precise product distribution, still, there is a compensating effect such that the total number of moles of all products formed tends to remain more constant than the product distribution in individual runs. A summary by carbon number is given in Table II.

It is important to realize that deviations from run to run are real, and not just analytical scatter. This latter

TABLE II

MOLES OF PRODUCT FOR EACH CARBON NUMBER FORMED PER 100 MOLES OF HEXADECANE CRACKED OVER A SILICA-ALUMINA CATALYST AT 372°

Carbon no.	Run number I	II	III	IV	V	VI	VII	VIII	IX	X	Av.	Av. dev.
1	0.5	0.6	1.0	0.7	0.9	0.4	1.1	0.7	0.2	0.8	0.7	0.2
2	4.2	5.8	3.0	5.2	4.0	5.5	4.4	6.6	5.6	6.2	5.1	0.9
3	86.9	111.3	90.8	87.6	89.2	104.7	111.6	102.4	88.3	92.2	96.6	8.9
4	141.3	152.0	146.6	153.0	176.5	171.2	165.6	182.6	178.6	163.7	163.1	11.9
5	73.9	69.2	83.0	66.8	68.7	75.9	60.1	58.1	70.3	53.7	68.0	6.6
6	21.4	21.6	20.6	21.4	13.5	...	17.5	12.4	23.7	15.2	18.5	3.5
7	17.0	15.2	17.5	13.2	11.6	...	15.8	10.0	14.0	12.6	14.1	2.0
8	6.3	5.5	7.3	6.5	4.5	...	6.2	4.8	7.2	6.7	6.1	0.8
9	1.2	1.4	1.5	2.5	1.4	...	2.4	2.0	2.2	2.9	1.9	.5
10	0.6	0.3	0.3	0.7	0.3	...	0.3	0.4	0.4	0.8	0.5	.2
11	0.9	1.2	1.3	2.9	1.0	...	1.1	0.4	1.2	1.7	1.3	.4
12 and 13	2.1	1.9	1.8	4.7	2.3	...	1.2	3.1	2.5	2.6	2.5	.7
											378.4	

is estimated at less than 5% and probably should be set at 2–3%. The actual deviations no doubt arise from slightly different flow rates and reactant partial pressures from run to run and from different process periods as well as the use of various tracers which could have a slight effect on the cracking reaction. The constancy of the total sum of all products (±3%) is a sound indication of good reproducibility in the analytical techniques as well as in the process conditions.

Other parts of Table I needing a few words of explanation are:

1. Peak no. 26 for normal heptane in run 10 was omitted from the averages because in this run the added radioactive heptane concentration is significant in comparison with all of the normal heptane formed during the reaction.

2. The time of contact is calculated as a time required for the flow through a volume of 37 cc. of catalyst at the observed temperature. The time is calculated without making any allowance for the volume of the catalyst particles themselves.

Discussion

Study of the differences observed between the present results and those reported by Greensfelder under different conditions led to the conclusion that Greensfelder's original method of calculation could be modified according to the line of reasoning set forth below. In a review article appearing in 1955,[4] Greensfelder summarized his estimates of the heats of formation of various gaseous alkyl carbonium ions. These are

TABLE III

HEATS OF FORMATION[a] OF CARBONIUM IONS FROM PARAFFINS[4]

Parent paraffins	Type of carbonium ions: Primary	Secondary	Tertiary
CH_4	315.5	...	...
C_2H_6	280.5	...	...
C_3H_8	265.5	249.5	...
n-C_4H_{10}	268.0	241.5	...
i-C_4H_{10}	263.0	...	233.0
n-C_5H_{12}	266.0	241.0	...
i-C_5H_{12}	263.0	...	228.0
$\geqslant n$-C_8H_{14}	266.0	241.0	...
$\geqslant i$-C_6H_{14}	263.0	...	228.0

[a] The energy values in kcal. per mole shown in colums 2, 3 and 4 are ΔH_{298} values for the reaction $CH_{2n+2} \rightarrow CH^+_{2n+1} + H^-$.

shown in Table III. They have been calculated from the ionization potential data of Stevenson[5] and thermodynamic data. They differ slightly from the earlier estimates of Evans and Polanyi.[6]

It is to be noted that the energies in Table III relate only to the heat of formation, ΔH^0_{298}, since the lack of entropy data precludes systematic establishment of the truly desired free energy values. The many striking parallelisms between the ΔH^0_{298} values and the rates and modes of reaction, however, provide justification for their use. Also one must remember that all values relate to the gaseous ions; energies of binding to the catalyst surface are not taken into account. Thus, it was assumed in what is to follow that although the energies must be very different on the surface still the energy differences between species remain the same on the surface as in the gas phase. Greensfelder has pointed out how these energy differences can be invoked to explain qualitatively the usual reactions of carbonium ions.[4] They have not, however, as yet been used in an actual calculation of product distributions.

Deferring, for the moment, discussion of the actual mode of formation of carbonium ions, we have, from Table III, energy values for the reactions

$$n\text{-}C_{16}H_{34} \longrightarrow 1^+\text{-}n\text{-}C_{16}H_{33} + H^- \qquad \Delta H = 266 \text{ kcal./mole}$$

$$n\text{-}C_{16}H_{34} \longrightarrow 2^+\text{-}n\text{-}C_{16}H_{33} + H^- \qquad \Delta H = 241.5 \text{ kcal./mole}$$

$$n\text{-}C_{16}H_{34} \longrightarrow 3,4\ldots 8^+\text{-}n\text{-}C_{16}H_{33} + H^- \qquad \Delta H = 241.0 \text{ kcal./mole}$$

where 1^+, 2^+, . . ., etc., are used to designate the position of the carbon atom on which the charge of the carbonium ion is located. The use of 241.5 kcal./mole for the energy of formation of the 2^+-secondary ion instead of setting this energy equal to the 3^+, 4^+, 5^+, . . ., secondary ions is questionable and has not been made previously. This figure was chosen by analogy of structure with the 2^+-n-C_4H_9 ion, 241.5 kcal./mole, and that for 3^+, 4^+, . . ., 8^+ by analogy with 3^+ and 4^+-n-C_6H_{13}.

Next we assume that the probability of forming any given ion is controlled by these energy differences through the Boltzmann distribution

$$g\,(3, 4, \ldots, 8^+\text{-}n\text{-}C_{16}H_{33}) = e^{-(241.0 - 241.0)/RT} = 1$$

$$g\,(2^+\text{-}n\text{-}C_{16}H_{33}) = e^{-(241.5 - 241.0)/RT} = 0.68 \text{ at } 372°$$

$$g\,(1^+\text{-}n\text{-}C_{16}H_{33}) = e^{-(266.0 - 241.0)/RT} = 3 \times 10^{-9} \text{ at } 372°$$

and normalize to find the actual fraction P_i of the ion of interest. (The authors realize that the temperature correction here made for product distribution is somewhat uncertain since the 0.5 kcal. difference between the 241.5 and 241 kcal. is only approximate. Furthermore, no separate calculation was carried out for the temperature term alone as compared to the corrections

(5) (a) D. P. Stevenson, *Trans. Faraday Soc.*, **49**, 1867 (1953); (b) *Discussions Faraday Soc.*, **10**, 35 (1951); and co-workers, *J. Am. Chem. Soc.*, **74**, 3269 (1952).

(6) A. G. Evans and M. J. Polanyi, *J. Chem. Soc.*, 252 (1947).

TABLE IV

MOLES FORMED PER 100 MOLES CETANE CRACKED

	Carbon number														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	Total
Obsd. (Greensfelder), 500°	5	12	97	102	64	50	8	8	3	3	2	2	2	1	359
Calcd. (Greensfelder)	0	0	95	97	72	41	7	6	5	4	4	4	4	0	339
Calcd. (present method) 500°	0	0	94.4	103.9	67.9	36.0	11.8	8.9	3.9	3.6	2.9	1.6	4.4	0	339.3

from tracer results for olefin cracking, alkylation and polymerization.)

At this point the further assumption is made that any given secondary carbonium ion is in statistical equilibrium with the tertiary ions produced from it by methyl migration of either end carbon atom. This assumption of extensive skeletal isomerization before cracking has been implied in the discussion of previous authors but never expressly made in their calculations. It is based on the following points:

1. Extensive isomerization (to approximate thermodynamic equilibrium) is known to occur with those substances which form carbonium ions easily. Hence if as postulated both olefin and paraffin cracking go through identical carbonium ions then the carbonium ions formed from paraffins must also extensively isomerize. This point is corroborated by a comparison of tracer data in experiments where heptane-1-C^{14} and heptene-1-C^{14} were added to the flow stream. Here although the reactions of heptene were much more extensive, still the ratio of activity in cracked products to activity in isomerized products is about the same (8.1 for heptene, 6.7 for heptane). Furthermore most of the isomeric activity was found in the methyl hexanes (1st paper[2]).

2. Previous work in the literature by Nickalaeva and Frost[7]; Hay, Montgomery and Coull[8]; and Petrov, Frost and Batuev[9] on *n*-hexene; by Berg, Sumner and Montgomery[10] on heptene; and by Petrov and Frost[11] on octene indicated that the overwhelming isomerization reaction in each case was that forming the monomethyl isomers, presumably caused by migration of a single methyl group. In this respect we note that the extremely high isobutane/*n*-butane product ratio observed in catalytic cracking has been rationalized on the basis of an extensive isomerization of normal precursors followed by cracking.[3]

The assumption of extensive carbonium ion skeletal isomerization then seems to be warranted; in fact, according to experimental work[3] on olefins, such isomerization goes to approximate thermodynamic equilibrium for carbon numbers six, seven and eight. The lack of data above the octanes makes an estimate of the isomeric ratios impossible on a thermodynamic basis. Thus it was necessary to assume statistical equilibrium between the normal and methyl isomers which indeed is a fair approximation to the high temperature thermodynamic equilibrium, at least for carbon numbers six, seven and eight.

The statistics were then taken on the basis

$$\frac{\text{number of ways of forming given isomeric ion from } i^{+}\text{-}n\text{-}C_nH_{2n+1}}{\sum_{\text{isomers}} \text{number of ways of forming given isomer (normal isomers of course included)}}$$

After the formation of a given secondary ion and isomerization of part of it to the corresponding tertiary methyl carbonium ions, β cracking was assumed to occur (only to fragments of three or more carbon atoms, *cf.* Table III) yielding in each case an olefin and a new smaller carbonium ion. If in any case cracking could occur to more than one set of products the fraction reacting *via* each pathway was calculated, as above, from the energy differences of the resulting carbonium ions (columns 2, 3 and 4, Table III) and the Boltzmann distribution. The carbonium ions formed in the primary step are assumed to isomerize and crack in successive stages according to the rules outlined above.

An estimation of the amount of secondary olefin cracking is possible at 372° from our integral reactor radioactive experiments. These experiments also allow an estimate of the amount of secondary alkylation and polymerization reactions at 372°. For runs at 500°, Greensfelder in his original calculation assumed that 50% of the olefins formed cracked in secondary reactions; he neglected secondary alkylation or polymerization reactions. We have shown that these latter are important at 372° and infer that they are also important at 500°. We have also shown that greater than 50% of heptene-1 cracks at 372° and would expect that at least as much secondary olefin cracking occurs at 500°. However, Greensfelder's neglect of alkylation and polymerization reactions is compensated by his low estimate of secondary olefin cracking. Since we had no quantitative estimate of either type of secondary reaction at 500° we have followed his lead for calculating the cracking of hexadecane at this temperature by assuming 50% secondary olefin cracking according to the rules set forth above. Accordingly, only our assumption of extensive skeletal isomerization and our introduction of temperature dependence are different from Greensfelder's assumptions in the calculation for 500°. Agreement, as seen in Table IV, is quite good.

At 372° the fraction of secondary *n*-olefin ($\geqslant C_6$) cracking was estimated as 0.8. This was based on the observed cracking activity of 1-heptene, a typical *n*-olefin, in the tracer experiments. Here 77% of the radioactive heptene added cracked and since cracking activity increases with chain length in any homologous series the rounded off figure of 0.80 seems reasonable. No correction of this figure for average reactor residence time was made because essentially all (98.5%) of the added heptene reacted to products other than *n*-heptane *and* unreacted 1-heptene by cracking, isomerization, or alkylation. This suggests that reaction is fast compared to residence time. All iso-olefins greater than C_6 were assumed to crack in secondary reaction. This assumption was made on the basis that the reactivity of iso-olefins is known to be considerably greater than that of the corresponding normal compounds. (Use of the above fraction, 0.8, in place of 1.0 for the iso-olefins does not greatly affect the calculated distribution; C_4 would drop by 7.6 moles, all other changes would be much less).

Finally, the results were corrected for the alkylation or polymerization reactions of propylene on the basis of direct observation with a tracer experiment. Here correction for the propylene concentration profile down

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(8) R. G. Hay, C. W. Montgomery and J. Coull, *Ind. Eng. Chem.*, **37**, 335 (1945).

(9) A. A. Petrov, A. V. Frost and M. I. Batuev, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 745 (1951); cited from *C. A.*, **46**, 4776*c* (1952).

(10) L. Berg, G. L. Sumner and C. W. Montgomery, *Ind. Eng. Chem.*, **38**, 734 (1946).

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TABLE V

COMPARISON OF OBSERVED AND CALCULATED PRODUCT DISTRIBUTION, MOLES PER 100 MOLES OF CETANE CRACKED

Carbon no.	Obsd. 372° av. 9 runs	Calcd. (372°) (uncorr. for alkylation and polymerization)	Alkylation and polymerization correction	Total (calcd.) corr.
1	0.7 ± 0.2	0	0	0
2	5.1 ± 0.9	0	0	0
3	96.6 ± 8.9	108.6	−22.3	86.3
4	163.1 ± 11.9	136.5	11.1	147.6
5	68.0 ± 6.6	74.8	3.5	78.3
6	18.5 ± 3.5	40.2	5.0	45.2
7	14.1 ± 2.0	7.6	1.6	9.2
8	6.1 ± 0.8	2.8	0.6	3.4
9	1.9 ± .5	0.7	.1	0.8
10	0.5 ± .2[a]	.6	.1	.7
11	1.3 ± .4	.5	.2	.7
12	2.5 ± .7	.2	.1	.3
13		.6	.0	.6
Total	378.4 ± 36.6 (375.7 ± 10.7)[b]	373.1		373.1

[a] The amount of C_{10} observed seems to be out of line with the other products. It is possible that some of its isomers have been hidden in other peaks and are thus not properly accounted for. [b] This sum is an average total over the 9 complete runs rather than the total of the figures in column II.

the bed was necessary and was made in accordance with our previous discussion (paper I) under the assumption that the maximum possible specific activity ratio of a secondary product to the propylene at the bed exit was 2. The observed specific activity ratios reported previously were used. The method by which the correction was made becomes apparent by examination of the discussion in the first paper of this series.

Propylene is by far the most important product to be considered for alkylation or polymerization since it is not only very reactive but is also present in far the highest concentration of all olefins. The neglect (for lack of tracer data) of other alkylation reactions is expected to give rise to some error in the results but they should still be accurate enough to indicate whether the calculation we have outlined above is a valid approach. The calculated and observed results for 372° are shown in Table V. Details of the calculations can be found in pages 175–194 of the thesis of Van Hook.[1]

The point in least agreement is that for carbon number six. Here the predicted value is more than a factor of two times the observed one. The discrepancy could be rationalized by the hypothesis that carbonium ion cracking is more rapid at this temperature than ion saturation by hydrogen abstraction. Thus since, by the β rule, the 3^+-*n*-hexyl ion will not crack and would not by the hypothesis saturate as rapidly as the 2^+-*n*-hexyl ion cracks, the equilibrium between the 2^+ and 3^+ ions would be disturbed and some 3^+-*n*-hexyl would rearrange to 2^+-*n*-hexyl which could in turn crack. Such behavior would be an important factor in the determination of the final amount of product only for carbon number six since higher homologs can crack from either position.

In summary, then, one can state that the introduction of temperature sensitive terms into the standard Greensfelder method of calculation of product distributions, and the use of experimental radioactive tracer results to correct for secondary reactions, enables one to obtain fairly good agreement between the observed and calculated distribution for cracking *n*-hexadecane at 372° over a silica–alumina catalyst.

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Activation Energies for Reorientation Processes in Ferrocene and Some of its Derivatives: A Study of Proton Magnetic Resonance Spectra

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A systematic study of the proton magnetic resonance spectra of ferrocene and some of its typical derivatives has been made over a wide range of temperature (78–300°K.) using a Pound-Knight-Watkins type oscillator and a special cryostat. The line width (δH) and the second moment $(\Delta H)^2$ data have been interpreted to elucidate the reorientation processes of the cyclopentadienyl rings and the influence of the substituents on such processes. Some derivatives with completely deuterated substituents were specially studied to eliminate any contribution to the absorption curves obtained for the protons. In general δH and $(\Delta H)^2$ have been shown to increase with increased substitution at corresponding temperatures; the broadening arising from interactions between the protons of the cyclopentadienyl rings and the nuclei of the substituents is also discussed. The plots of δH *vs.* temperature have been used to evaluate the correlation time τ_c at certain temperatures. The magnitudes of the activation energy E_a for the reorientation processes have been calculated therefrom. These range from 2.3 kcal./mole for ferrocene to 5.0 kcal./mole for diperdeuterioacetylferrocene and are seen to increase with increasing substitution in one or both rings.

The first reference to the possibility of "rotation" of one cyclopentadienyl ring with respect to the other was reported by Woodward, *et al.*[2] These investigators had prepared the diacetyl and dicarboxylic acid derivatives of ferrocene and were considering from the structural point of view whether the barrier in the way of "rotation" of one ring with respect to the other is sufficient to permit the existence of heteroannular isomers. Richmond and Freiser[3] studied the dipole moments of mono- and diacetylferrocene as a means of obtaining experimental evidence for the free rotation of the cyclopentadienyl rings in ferrocene. The electron diffraction study of ferrocene by Seibold and Sutton[4] indicates that in the vapor state the cyclopentadienyl rings rotate freely about the common orthogonal axis. Molecular orbital treatments[5,6] of ferrocene suggest that no

(1) (a) The author wishes to thank the Research Corporation and the Monsanto Research Laboratory for supporting this work. He is also thankful to Dr. M. Rausch of this Laboratory and Professor R. B. Woodward of Harvard University for supplying some of the derivatives of ferrocene. Any inquiries and requests for reprints after Sept. 1, 1963, should be addressed to this author at Pennsylvania State University, University Park, Pa. (b) Predoctoral research fellowships were made available to this author by the Ethyl Corporation (1961–1962) and the National Science Foundation (Summer 1961). The author is thankful to them for these fellowships.

(2) R. B. Woodward, M. Rosenblum and M. C. Whiting, *J. Am. Chem. Soc.*, **74**, 3458 (1952).

(3) H. H. Richmond and H. Freiser, *ibid.*, **77**, 2022 (1955).

(4) E. A. Seibold and L. E. Sutton, *J. Chem. Phys.*, **23**, 1967 (1955).

(5) (a) H. H. Jaffé, *ibid.*, **21**, 156 (1953); (b) W. Moffitt, *J. Am. Chem. Soc.*, **76**, 3386 (1954).