Nuclear Magnetic Resonance Studies of Keto–Enol Equilibria. IV. Naphthalene Derivatives

By Gerald O. Dudek

The proton resonance spectra of compounds obtained from a 1:1 condensation of monoamines with hydroxyacetonaphthones or hydroxynaphthaldehydes have been measured. Tautomerization in these compounds has been assessed by means of the presence or absence of spin–spin coupling of the acidic proton with the α-protons of the amines. The condensation products of 1-hydroxy-2-acetonaphthone and 2-hydroxy-1-naphthaldehyde are keto-amines, while the condensation products of the other aromatic hydroxy-carbonyl compounds are probably the expected phenol-imines. A long-range spin–spin coupling of 1.4 c.p.s. between the methyl and

the α-protons of the amine in the $CH_3C{=}NCH_2R$ groups has been observed in Schiff bases derived from one hydroxyacetonaphthone.

Previous papers in this series[1,2] have discussed tautomerization in condensation products of aliphatic amines with aliphatic β-diketones such as acetylacetone. The evidence obtained from n.m.r. spectral analysis indicates that in solution these adducts are best represented as being enolized with the acidic proton attached to nitrogen (1). The energy barrier between 1 and either the un-enolized Schiff base or the enol–imine tautomer with the proton on oxygen is quite large. The latter conclusion is based on the absence
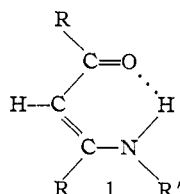
of either solvent or substituent effects (varying both R and R') upon the observed equilibrium.[2] Accordingly, other systems related to the ones previously studied are being investigated in order to determine the stability of the keto-amine form (1) over the other possible tautomers.

As a guide in this search, Wheland's thermodynamic estimates of the difference in stability of the keto vs. the enol forms of several ketones are useful.[3] Some of his data are listed in Table I. The energy difference between the two tautomers is appreciably smaller in the naphthalenes than in either acetone or phenol.

TABLE I

THE TOTAL ENERGY OF THE KETO FORM MINUS THAT OF THE ENOL FORM OF SOME CARBONYL COMPOUNDS

	Kcal.
Phenol	−18
1-Naphthol	−10
2-Naphthol	−10
Resorcinol	− 5
Acetone	+13

Thomson[4,5] proved that several dihydroxynaphthalenes have small energy barriers to the keto–enol conversion: For example, with 1,4-dihydroxynaphthalene, the keto and enol forms (2 and 3, respectively) are of comparable stability since a melt of this compound consists of 10% of the diketo form. It was also found that the diketo form is present in observable concentrations only in those naphthalenes which do not make the second ring quinoid in forming the carbonyl tautomer.
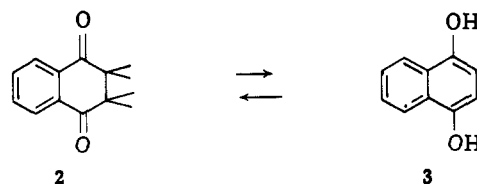
The arylazonaphthalenes[6-8] are another system in which the keto–enol equilibrium constant is near unity
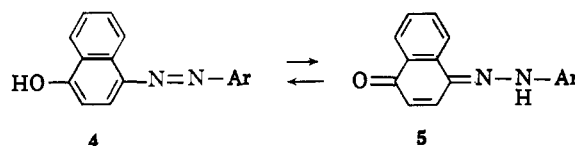
Substituents in either the naphthalene or benzene ring can alter the amount of each form present, and the effect of solvents upon the equilibria parallels the solvent dependence of the keto–enol equilibria of ethyl acetoacetate and acetylacetone.

Condensation products of amines with hydroxyacetonaphthones and hydroxynaphthaldehydes have been synthesized. The proton resonance spectra of these compounds have been measured and the tautomeric species present thereby determined.[9] The stability of the amine over the imine form of the Schiff base is large enough in several cases to compensate for the loss of the resonance energy of one of the aromatic rings of the naphthalene. Therefore, in several instances the compounds are keto-amines. A surprising long-range coupling appearing in one member of the series is also discussed.

Experimental

Solvents.—The solvents were commercial reagent materials. Deuteriochloroform was supplied by Merck, Sharpe and Dohme of Canada.

Compounds.—The compounds used in this study have hitherto not been described. They all were formed from the amine and the hydroxycarbonylnaphthalene by previously described procedures.[2] The ones melting below 155° could be purified by sublimation and crystallization, while the higher melting were purified by crystallization. The appropriate physical quantities are listed in Table II.

Spectra.—Spectra were obtained on a Varian A-60 spectrometer operating at 60 Mc. Line positions were determined by an interpolation method using an audio oscillator monitored by a frequency counter and are accurate to ±0.3 c.p.s. or 0.005 p.p.m. at 60 Mc. except when the band width precluded such accuracy. The sample temperature[10] was 31°.

Solutions.—Solutions were prepared as previously described[1] using tetramethylsilane as the internal zero of reference. Concentrations were approximately 0.5 M unless otherwise stated.

(1) G. O. Dudek and R. H. Holm, J. Am. Chem. Soc., **83**, 2099 (1961).

(2) G. O. Dudek and R. H. Holm, ibid., **84**, 2691 (1962).

(3) G. W. Wheland, "Advanced Organic Chemistry," 3rd ed., John Wiley and Sons, Inc., New York, N. Y., 1960, p. 669.

(4) R. H. Thomson, J. Chem. Soc., 1950 (1937); D. B. Bruce and R. H. Thomson, ibid., 2759 (1952).

(5) I wish to thank R. F. Hutton for calling attention to this work and for a discussion of his confirmatory n.m.r. studies.

(6) A. Burawoy and A. R. Thompson, J. Chem. Soc., 1443 (1953).

(7) E. Sawichi, J. Org. Chem., **22**, 743 (1957).

(8) K. J. Morgan, J. Chem. Soc., 2151 (1961), and references cited therein.

(9) A preliminary account of this work has appeared: G. O. Dudek and R. H. Holm, J. Am. Chem. Soc., **83**, 3914 (1961).

(10) Several values for resonance positions listed in ref. 9 differ slightly from those in Table III. The shift is a result of a change in the sample temperature.

TABLE II

PHYSICAL PROPERTIES OF THE SCHIFF BASES[11]

Compound[11]	Color[a]	M.p., °C.	Carbon, %		Hydrogen, %		Nitrogen, %	
			Calcd.	Found	Calcd.	Found	Calcd.	Found
N-Methyl-1-hydroxy-2-acetonaphthone-imine	Y	144.4–145.2	78.36	78.52	6.58	6.67	7.03	7.02
N-Benzyl-1-hydroxy-2-acetonaphthone-imine	Y	149.8–150.6	82.87	82.72	6.22	6.37	5.09	5.15
N-Methyl-6-hydroxy-2-acetonaphthone-imine	W	178–180 dec.	78.36	78.26	6.58	6.64	7.03	7.07
N-Methyl-3-hydroxy-2-acetonaphthone-imine	O	139.8–141.0	78.36	78.39	6.58	6.64	7.03	7.07
N-Methyl-2-hydroxy-1-acetonaphthone-imine	W	179.2–179.8	78.36	78.16	6.58	6.68	7.03	7.24
N-Methyl-2-hydroxy-1-naphthaldehyde-imine	Y	132.0–132.6	77.81	77.70	5.99	5.97	7.56	7.54
N-Benzyl-2-hydroxy-1-naphthaldehyde-imine	Y	99.4–100.6	82.73	82.46	5.79	5.66	5.36	5.41
N-Benzyl-2-hydroxyacetophenone-imine	Y	117.8–118.2	79.97	79.77	6.71	6.80	6.22	6.41

[a] Y = yellow; W = white; O = orange.

TABLE III

PROTON RESONANCE DATA FOR THE AROMATIC SCHIFF BASES IN P.P.M. RELATIVE TO TETRAMETHYLSILANE

Compound,[11] imine	Solv.			
N-Methyl-1-hydroxy-2-acetonaphthone-	CDCl₃	2.25	3.08(4.4)[a]	15.9
	C₆H₆	1.40	2.16(2.6)	16.5
	Pyridine	2.09	2.83(4.6)	16.2
N-Benzyl-1-hydroxy-1-acetonaphthone-	CDCl₃	2.37	4.67(4.8)[b,c]	16.4
	C₆H₆	1.54	3.94(3.2)	17.1
	Pyridine	2.39	4.72(5.0)	16.5
N-Methyl-6-hydroxy-2-acetonaphthone-[d]	Pyridine	2.17(0.8)	3.35	[e]
N-Methyl-3-hydroxy-2-acetonaphthone-	CDCl₃	2.29(0.7)[f]	3.29	15.3
	CCl₄	2.22(0.8)	3.25	14.2
	Pyridine	2.15(0.8)	3.09	15.5
N-Methyl-2-hydroxy-1-acetonaphthone-	CDCl₃	2.53	3.18	13.8
	Pyridine	2.38		
		2.57(1.4)[g]	3.02,3.18(1.4)[g,e]	
N-Benzyl-2-hydroxy-acetophenone-	0.2 M CDCl₃	2.38	4.77	16.3
	.4 M CDCl₃	2.34	4.74	16.3
	.2 M CCl₄	2.29	4.71	15.1
N-Methyl-2-hydroxy-1-naphthaldehyde-	CDCl₃	8.59(7.8)[b]	3.29	14.3
	Pyridine	[e]	3.12	14.8
N-Benzyl-2-hydroxy-1-naphthaldehyde-	CDCl₃	8.81(5.9)	4.72	14.7
N-Benzyl-salicylaldehyde-	CCl₄	8.34	4.75	12.7

[a] J in c.p.s. [b] To a singlet upon deuteration of the acidic proton. [c] 4.7 c.p.s. at 15.1 Mc. [d] Insoluble in CDCl₃. [e] Not located. [f] Unaffected by deuteration of the acidic proton. [g] Quartet.

Results

The spectra of the condensation products of amines with 1-hydroxy-2-acetonaphthone (6) possessed doublets (Table III) for the benzyl and methyl signals (Fig. 1). As with the aliphatic bases previously studied,[1,2] the acidic proton is assumed to be residing on the nitrogen with a long exchange time to oxygen, and the methyl and benzyl groups (R=H, C₆H₅) coupled to this proton with $J \approx 5$ c.p.s. This is true spin–spin coupling since the doublet collapses upon deuteration (Fig. 1) of the acidic proton, the magni-

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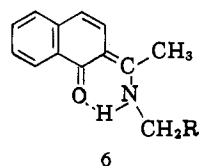
tude of the coupling is field invariant (measured at 15 and 60 Mc.), and is present with both the methyl and benzyl derivatives. Any possibility of the doublet being due to either a chemical shift or to rotational isomers is definitely eliminated. The compound is therefore a *keto-amine*. The formation of this tautomer involves the loss of most of the resonance energy of one of the aromatic rings of the naphthalene system.

In chloroform solution, a coupling of 4.8 c.p.s. requires that the exchange time to oxygen of the amine

(11) These compounds are described as derivatives of the hydroxyketone or aldehyde. This does not imply which tautomeric form is present in solution. The generic term Schiff base for these compounds likewise does not imply structure.

proton be greater than ~0.03 sec.[12] Whether the proton resides in a single or a double potential minimum cannot be answered at present, but on the basis of evidence from other systems a double minimum is favored.[13] The line broadening occurring when the substituent (R) is changed from methyl to benzyl (see Fig. 1), the solvent dependence of the coupling, and the smaller splitting observed ($J = 4.4$–4.8 c.p.s.) between the α-protons of the amine and the acidic hydrogen suggest that exchange of the acidic proton, although slow, may be far more important in these compounds than with the aliphatic Schiff bases (where $J \approx 5.1$–6.8 c.p.s.).
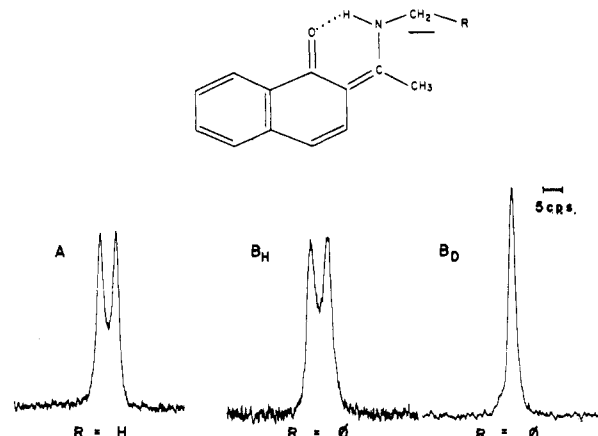

Fig. 1.—The proton resonance spectrum of: A, the N-methyl hydrogens in N-methyl-1-hydroxy-2-acetonaphthone-imine (in CDCl₃ soln. at 60 Mc.); B$_H$, the N-benzyl hydrogens in N-benzyl-1-hydroxy-2-acetonaphthone-imine (in CDCl₃ soln. at 60 Mc.); B$_D$, the N-benzyl hydrogens with the acidic proton deuteriated.

In the aldehydes, the N-methyl and the N-benzyl signals are broadened, but not split (Fig. 2) and the aldehydic proton is a broad doublet. Since the *trans* coupling of an aldehydic proton to the proton on nitrogen is larger than the *cis* coupling of the amino proton to an alkyl group,[14] the acidic proton exchanging between oxygen and nitrogen will collapse the doublet from the methyl before collapsing the doublet from the aldehydic signal. Upon deuteration of the acidic proton, the methyl signal narrows and the aldehyde doublet becomes a singlet. The compound is the keto-amine tautomer, but with a faster rate of exchange of the acidic proton between sites.

Since 1-hydroxy-2-acetonaphthone gave rise to Schiff bases where the keto-amine form was of greater stability, the spectrum of the reverse isomer, N-methyl-2-

(12) J. A. Pople, W. G. Schneider and H. J. Bernstein, "High-resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, chap. 10.

(13) J. Dabrowski, *Bull. Acad. Poln. Sci., Ser. Sci., Chim., Geol. et Geograph.*, 1, 93 (1959).
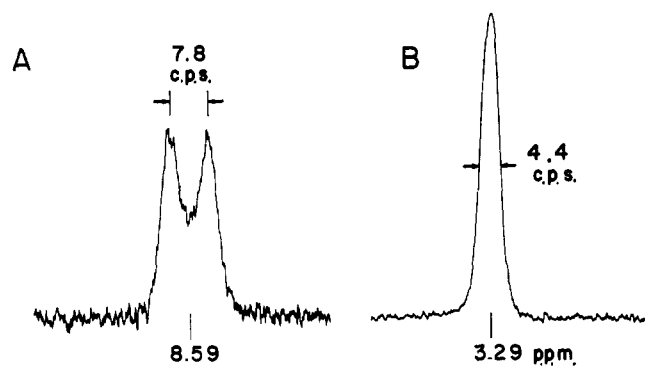
(14) G. Dudek, unpublished results.

Fig. 2.—The proton resonance signals of: A, the aldehydic hydrogen; B, the methyl hydrogen in N-methyl-2-hydroxy-1-naphthaldehyde-imine (CDCl₃ soln. at 60 Mc.).

hydroxy-1-acetonaphthone-imine, was investigated. In contrast to the 1-hydroxy-2-acetonaphthone condensation products (6), the N-methyl or N-benzyl signals were singlets (Fig. 3) in chloroform solution.

Electronically, the compound should have the same barrier to tautomeric interconversion as do the adducts of 1-hydroxy-2-acetonaphthone. The difference in resonance energy of having either the carbonyl or the exocyclic double bond adjacent to the intact aromatic system should be small.[15] The Schiff bases from 2-hydroxyl-1-naphthaldehyde, where a proton replaces the bulky methyl group in the side chain, as well as the studies on arylazonaphthalenes,[6-8] support this contention.

In deuteriochloroform solution, N-methyl-2-hydroxy-1-acetonaphthone-imine has two sharp methyl resonances at 2.53 and 3.18 p.p.m. (Fig. 3) which is consistent with its structure and also with the other members of the series. However in pyridine solution the spectrum is greatly altered—four methyl signals are present, two of them being quartets with $J = 1.4$ c.p.s. (Fig. 3). With the benzyl derivative, the four signals are present in pyridine solution; the additional signal from the acetomethyl group is a triplet, while the one from the benzyl is broadened but not resolved.

If it is assumed that pyridine weakens the hydrogen bond by association with the acidic hydrogen, two forms of the molecule can be present in solution
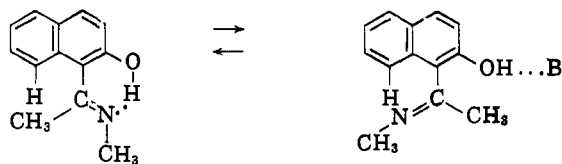
Since conjugation of the imino group with the aromatic system is important, interconversion between these rotamers can be slow; thus two bands for each methyl will be present.

The failure to observe the rotamers with the other Schiff bases in pyridine solution may be a reflection of the stronger hydrogen bonds in these compounds. The fine structure observed in these peaks can only arise from a long-range coupling between the methyl protons or between the methyl and benzyl protons. The substitution of a benzyl for a methyl on the nitrogen altered the acetomethyl resonance (at 3.2 p.p.m.) from a quartet to a triplet consistent with this viewpoint. The magnitude of the coupling is quite large considering the number of bonds involved.

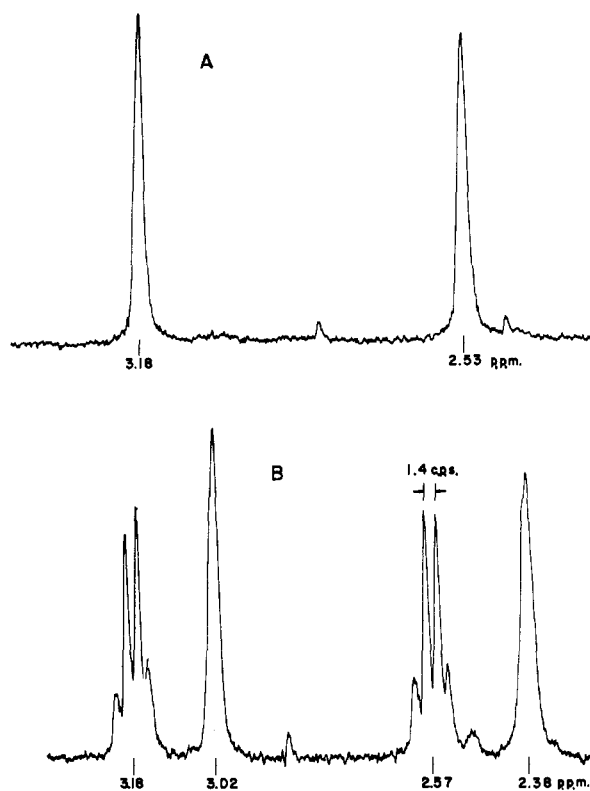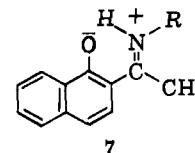Schiff bases formed from benzylamine and either salicylaldehyde or o-hydroxyacetophenone have the

(15) G. W. Wheland, "Resonance in Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1955, pp. 98–99.

Fig. 3.—The methyl proton resonance signals (at 60 Mc.) of N-methyl-2-hydroxy-1-acetonaphthone-imine in: A, CDCl₃ soln.; B, pyridine soln.

expected phenol-imine structure as the benzyl signals are sharp singlets (Table III). The loss of 30 kcal. of resonance energy in forming the keto-amine tautomer is not compensated by the stability of the keto-amine over the phenol-imine form.[2] The differences in properties of the salicylaldehyde Schiff base and the acetophenone base are quite striking. Not only is the melting point of the ketone base about 100° higher than that of the aldehyde,[2] but the hydrogen bond in the former is much stronger.

Both 3-hydroxy-2-acetonaphthone and 6-hydroxy-2-acetonaphthone yielded condensation products with methylamine which were apparently phenol-imines. These compounds gave rise to methyl resonances which were sharp singlets.

Discussion

The presence of the keto-amine form as the stable tautomer in the condensation products of amines with 1-hydroxy-2-acetonaphthone and 2-hydroxy-1-naphthaldehyde is further evidence for the greater stability of the –NH vs. the –OH form in Schiff bases.[2] The formation of the amine tautomer 6 involves an appreciable loss in the resonance energy of one of the aromatic rings as the compound is essentially an o-quinone.[16] With a naphthalene system, the loss of resonance energy of one aromatic ring would amount to about 20–24 kcal.[15] However, the decrease in resonance stabilization will be smaller in the Schiff bases due to contributions from polar forms such as 7.

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(16) Wheland[15] does not list a value for an o-quinone. However, 1,4-benzoquinone possesses only 4 kcal. of resonance energy.

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 in the 8-position of the ring is in agreement with this assumption.[18]

(17) J. A. Elvidge and L. M. Jackman, *J. Chem. Soc.*, 859 (1961).

(18) An analysis of the shifts of the aromatic protons of the naphthalene in the Schiff bases, the parent hydroxy carbonyl compounds, and a few model systems support this view. This study will be published in detail shortly. See also G. Dudek, *Spectrochim. Acta*, in press.

(19) M. Karplus, *J. Chem. Phys.*, **33**, 1842 (1960).

(20) M. P. Cava and J. P. van Metea, *J. Am. Chem. Soc.*, **84**, 2008 (1962).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, THE JOHNS HOPKINS UNIVERSITY, BALTIMORE 18, MARYLAND]

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

BY W. ALEXANDER VAN HOOK[1] AND PAUL H. EMMETT

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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 C₄ hydrocarbons. Approximately 160 moles of C₄ per 100 moles of hexadecane cracked was observed at 372° compared with about 100 moles per 100 moles of hexadecane at the higher tempera-ture. 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.