[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF TEXAS]

The Ionization Constants of a Number of Methylated Quinolines and of Certain Saturated Bases Isolated from Petroleum Distillates

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During an investigation dealing with extraction and identification of nitrogen bases[1] from petroleum distillates, it seemed worth while to determine the ionization constants of all the monomethylquinolines and of some of the higher homologs. All of the bases identified so far from petroleum distillates belong to the series just mentioned. It seemed desirable to ascertain any order, if such existed, in the variation of these constants with the location of the methyl radicals in the quinoline nucleus; it was also desirable to know the relative strengths of the aromatic and non-aromatic petroleum bases, since such information might be of value in devising a scheme of separating the two types of bases found in petroleum distillates.

The method adopted for this investigation was the electrometric determination of the $[H^+]$ produced by the hydrolysis of the perchlorates of the bases under consideration. Use was made of an accurate potentiometer set-up, a saturated calomel half-cell, and a platinum wire in conjunction with quinhydrone. The calomel electrode was standardized by measurement against a 0.05 N potassium acid phthalate buffer solution, the P_{H} of which was known. In the P_{H} determinations of the quinolines, the potentials were reproducible to 0.0002–0.0005 volt; a change of platinum electrodes did not alter the observed voltage. All determinations were made at $25 \pm 0.05°$. The method was based upon the hydrolytic reaction of the base perchlorates, $B^+ + HOH \rightleftharpoons BOH + H^+$. The relation, readily deduced theoretically, for the calculation of the ionization constants is

$$K_{\text{I}} \text{ of Base} = K_{\text{w}} \cdot [B^+]/[H^+]^2$$

where K_w is the ionization constant of water. If the assumption is made that the $[B^+] = C$, the total salt concentration (an assumption very nearly true if the salt of a highly ionized acid, such as perchloric, is employed), the relation becomes

$$K_{\text{I}} \text{ of Base} = K_{\text{w}} \cdot C/[H^+]^2$$

This latter relation was used to calculate the ionization constants listed in the table. All materials were repurified for this investigation; after conversion into perchlorates, the salts were further purified by recrystallization from water.

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(1) This investigation is a continuation of A. P. I. Project 20, under the general direction of Prof. J. R. Bailey. The work begun under this project is now being aided by the Union Oil Company, which is furnishing the nitrogen base concentrates.

THE IONIZATION CONSTANTS OF SOME RELATED NITROGEN BASES

Base	Source	(*E*)obs.	Calcd. P_H	$K_I \times 10^9$
Quinoline	Eastman	0.2518	3.40	0.63
2-Methylquinoline	Synthetic[a]	.2336	3.71	2.64
3-Methylquinoline	Synthetic[a]	.2418	3.57	1.38
4-Methylquinoline	Eastman	.2405	3.60	1.59
5-Methylquinoline	Synthetic[a]	.2574	3.31	0.42
6-Methylquinoline	Synthetic[a]	.2482	3.46	.83
7-Methylquinoline	Synthetic[a]	.2437	3.54	1.20
8-Methylquinoline	Synthetic[a]	.2585	3.30	0.40
2,3-Dimethylquinoline	Petroleum[b]	.2479	3.47	.87
2,4-Dimethylquinoline	Petroleum[b]	.2426	3.56	1.32
2,6-Dimethylquinoline	Synthetic[a]	.2326	3.73	2.88
2,7-Dimethylquinoline	Synthetic[a]	.2458	3.51	1.04
2,8-Dimethylquinoline	Petroleum[b]	.2730	3.05	0.13
2,3,8-Trimethylquinoline	Petroleum[b]	.2630	3.21	.26
2,4,8-Trimethylquinoline	Petroleum[b]	.2617	3.24	.30
$C_{16}H_{25}N$ (a satd. base)	Petroleum[c]	.2417	3.57	1.38
$C_{13}H_{21}N$ (a satd. base)	Petroleum[c]	.2209	3.93	7.26

[a] Products synthesized and purified in this Laboratory. [b] Products extracted from petroleum distillates, purified and identified in this Laboratory. [c] Products extracted from petroleum, purified, but constitution yet to be determined.

The correlation between activity (as expressed by the ionization constant) and the location of the methyl radical is not striking. In the monomethylquinoline series, the location of the methyl radical on the nitrogen ring seems to have a larger influence upon the ionization constant than does location on the benzene ring, the decreasing order locations being 2, 4, 3. In this series, also, the 7-position of the benzene ring seems to produce the largest activity. The 2,6-position produces the greatest activity of the dimethylquinolines.

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