TABLE I

COMPARISON OF PHYSICAL PROPERTIES OF CONVENTIONAL AND MACRORETICULAR ION EXCHANGE RESINS

Resin	Form	Moisture holding capacity, % H_2O	Surface area, sq. meters/g. of dry resin	Apparent density,[a] g./ml.	True skeletal density,[b] g./ml.	Porosity (*P*), ml./ml.	Av. pore diam., Å.
Amberlyst 15	Na^+	50	42.5	1.012	1.513	0.319	288
Amberlite IR-120	Na^+	46	<0.1	1.489	1.518	.018	
Amberlyst XN-1001	Cl^-	60	62.9	0.559	1.136	.508	645
Amberlite IRA-400	Cl^-	45	<0.1	1.136	1.140	.004	

[a] Mercury displacement. [b] Helium displacement.

as a result of a collapse of the gel structure. The macroreticular resins, on the other hand, possess a non-gel pore structure that does not collapse on drying. Electron microscopic examination of ground, dry samples reveals no internal pore structure for the conventional resin and a definite pore structure for the macroreticular resins.

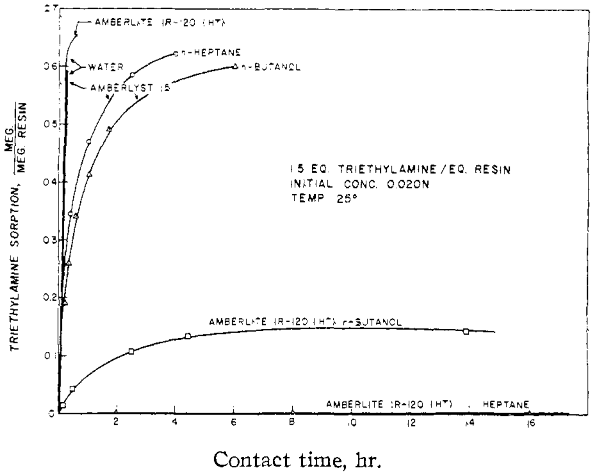

Fig. 1.—Rates of sorption of triethylamine by Amberlyst 15 and a conventional resin in various solvents.

The exchange kinetics of the Amberlyst 15 were compared with the conventional Amberlite IR-120 by studying the sorption of triethylamine from various solvents by the thoroughly dried hydrogen forms of the resin. The data (Fig. 1) show a remarkable difference in behavior between the two resins for solvents of low dielectric strength.

The difference between the macroreticular and conventional gel resins was noted further when the catalytic activities of the acid forms of Amberlyst 15 and Amberlite IR-120 were compared for the acid catalyzed decomposition of *tert*-butyl acetate into isobutylene and acetic acid at 25°. Thoroughly dried resins of the same particle size were compared. After 1 hour, the Amberlyst 15 activity was such that 80% of the equilibrium conversion was obtained and less than 1% was observed for the run with the Amberlite IR-120.

A similar catalytic study was conducted on the same resins for the reaction involving the synthesis of *tert*-butyl methacrylate from isobutylene and methacrylic acid at 0°. The two resins were compared by following the degree of conversion of the acid as a function of time. The data reveal the same difference in catalytic activity as noted in the *tert*-butyl acetate reaction. With Amberlyst 15, 50% conversion was achieved in 4 hours and less than 1% conversion was noted with Amberlite IR-120 in the same time interval.

Detailed studies on the chemical, physical, and catalytic properties of these macroreticular ion exchange polymers are in progress.

RESEARCH LABORATORIES ROBERT KUNIN
ROHM & HAAS COMPANY ERICH MEITZNER
PHILADELPHIA, PA. NEWMAN BORTNICK

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HYDROGEN TRANSFER BETWEEN A PHENOL AND ITS PHENOXY RADICAL[1]

Sir:

The rate of transfer of an atom of hydrogen between a diamagnetic molecule RH and the paramagnetic radical R· may be determined either through measurements of the broadening of e.s.r. lines of R· or n.m.r. lines of RH. Preservation of the hyperfine structure of the e.s.r. spectrum of R· insures that the broadening of n.m.r. lines of nuclei in RH (except for the transferred hydrogen) yields a direct measure of the rate.[2] The condition is fulfilled for the transfer of hydrogen between 2,4,6-tri-*tert*-butylphenol and the corresponding phenoxy radical. The n.m.r. spectrum of a solution of the phenol in carbon tetrachloride consists of the expected four lines. The lines are about 0.4 cycle per second broad with no resolved spin–spin splittings. Addition of the phenoxy radical broadens all lines, the ring and butyl lines equally and the hydroxyl line less. With increasing temperature the ring and butyl lines become broader, while the hydroxyl line becomes narrower. The line of tetramethylsilane which had been added to the solution is also broadened as the concentration of radical is increased but always much less than the butyl or ring lines.

In the analysis of the data the effect of the nonspecific dipolar broadening was allowed for, perhaps inaccurately, by subtraction of the breadth of the tetramethylsilane line. Since the correction is small compared with the large broadenings no great error is introduced into the over-all rates, but considerable uncertainty may be attached to the remarks in the final paragraphs concerning intermediate states.

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(1) This investigation was supported in part by Research Grant No. A-3054 of the National Institutes of Health, United States Public Health Service.

(2) H. McConnell and S. Berger, *J. Chem. Phys.*, **27**, 230 (1957).

Determination of the rate and order of the reaction from broadening of the ring and butyl lines is straightforward. The reaction is second order with $k = 300\ M^{-1}$ sec.$^{-1}$ at 30°; the activation energy is 1.0 ± 0.5 kcal. per mole.

The principal point of interest is the possibility of detecting properties of an intermediate through the magnetic behavior of the hydroxyl proton. The initial and final magnetic environments of an hydroxyl proton undergoing transfer are identical. Broadening of its resonance would be produced by a sufficiently strong magnetic pulse in transit. Application of the theory of McConnell and Berger,[2] or in the limit of weak impulses of a random walk model,[3] or the appropriate modification of BPP theory[4] lead to the same result. For pulses of duration τ each accompanied by a frequency shift δ the contribution to $1/T_2$ is $kc(2\pi\delta\tau)^2[1 + (2\pi\delta\tau)^2]^{-1}$ where k is the rate constant and c the concentration of radical. Under the previously mentioned assumption, values of $2\pi\delta\tau$ ranging from 0.4 ± 0.1 at 60° to 0.7 ± 0.1 at 27° were obtained. If δ corresponds to a splitting of twenty gauss in the intermediate, the duration of the intermediate is $\tau = 1 \times 10^{-9}$ sec. at 60° and $\tau = 2 \times 10^{-9}$ sec. at 27°.

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(5) Shell Fellow for 1961–1962.

DEPARTMENT OF CHEMISTRY
WASHINGTON UNIVERSITY ROBERT W. KREILICK[5]
SAINT LOUIS, MISSOURI S. I. WEISSMAN

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VALENCE BOND INTERPRETATION OF THE ADDITIVITY RELATION FOR C^{13}-PROTON COUPLING IN SUBSTITUTED METHANES[1]

Sir:

Several additivity relations have been pointed out recently[2–4] for the internuclear coupling constants observed in high resolution n.m.r. spectra. One involves the constancy of the three H–H coupling constants in monosubstituted ethylenes.[2] Another concerns the additivity of substituent effects upon the C^{13}–H coupling in substituted methanes.[4] Such observations are of considerable potential value to valence theory, but thus far detailed interpretations of the results have not appeared. The case of the monosubstituted ethylenes is the least tractable because it includes three H–H coupling constants, which originate in small deviations from the perfect pairing electronic structure. The coupling between directly bonded nuclei, such as C^{13}–H, is simpler to treat inasmuch as it depends almost entirely upon the perfect pairing structure.[5,6] The main purpose of this note is to report that by taking advantage of the latter aspect, and by making certain other reasonable approximations, we have developed a simple interpretation of the additivity relation for J_{CH}.

Malinowski's results[4] for the substituted methanes CHXYZ, may be summarized as

$$J_{\mathrm{CH}}\ (\mathrm{CHXYZ}) = \zeta_{\mathrm{X}} + \zeta_{\mathrm{Y}} + \zeta_{\mathrm{Z}} \qquad (1)$$

where ζ_{X} is a numerical constant for substituent X, determined from experiment as

$$\zeta_{\mathrm{X}} = J_{\mathrm{CH}}(\mathrm{CH_3X}) - (2/3)J_{\mathrm{CH}}(\mathrm{CH_4}) \qquad (2)$$

Our interpretation is based on the correlation which has been found[6–8] between J_{CH} and the s character of the carbon orbital used in the C–H bond.

For methane, a valence bond adaptation[6] of Ramsey's general formulation[9] has shown that the Fermi contact term governs J_{CH}. Moreover, the calculation made of the C^{13}–H coupling[6] gives J_{CH} to be a function primarily of λ, a parameter related to the C–H bond polarity. Upon extension of this approach to the substituted methanes we find that

$$J_{\mathrm{CH}}(\mathrm{CHXYZ}) = A\eta^2\alpha_{\mathrm{H}}^2/\Delta E \qquad (3)$$

where A is a collection of constants, ΔE is the average excitation energy,[9] and η is the normalization constant of the perfect pairing ground state wave function

$$u(\mathrm{i,j}) = \eta[\phi_{\mathrm{C}}(\mathrm{i})\phi_{\mathrm{H}}(\mathrm{j}) + \phi_{\mathrm{H}}(\mathrm{i})\phi_{\mathrm{C}}(\mathrm{j}) + \lambda\phi_{\mathrm{C}}(\mathrm{i})\phi_{\mathrm{C}}(\mathrm{j})] \qquad (4)$$

The quantity α_{H}^2 is the fractional 2s character of the carbon hybrid orbital

$$\phi_{\mathrm{C}} = \alpha s_{\mathrm{C}} + \sqrt{1 - \alpha^2}\ p_{\sigma_{\mathrm{C}}} \qquad (5)$$

used in the C–H bond. To a good approximation, Eq. (3) reduces to

$$J_{\mathrm{CH}}(\mathrm{CHXYZ}) \approx J_0\alpha_{\mathrm{H}}^2 = 4J_{\mathrm{CH}}(\mathrm{CH_4})\alpha_{\mathrm{H}}^2 = 500\alpha_{\mathrm{H}}^2 \text{ c.p.s.} \qquad (6)$$

because ΔE is not very sensitive to substituents and we have found that η, which depends upon α_{H} and λ, is nearly constant for the ranges of α_{H} and λ involved.

Two additional assumptions are required. The first is that all of the carbon 2s orbital is used in forming the C–H, C–X, C–Y and C–Z bonds, or

$$\alpha_{\mathrm{X}}^2 + \alpha_{\mathrm{Y}}^2 + \alpha_{\mathrm{Z}}^2 + \alpha_{\mathrm{H}}^2 = 1 \qquad (7)$$

The second concerns the manner in which a substituent perturbs the distribution of the carbon 2s orbital among the four bonds. As a model, consider the latter to be four interconnected potential wells for the 2s electron. In CH$_4$ the wells are of the same shape and depth and thus contain the same fraction of the 2s electron, $\alpha_{\mathrm{H}}^2(\mathrm{CH_4}) = 1/4$. Introduction of a substituent X changes the "depth" of the corresponding well by an effective,

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