addition of the dissociation constant for *o*-fluorophenol from Bennett, Brooks and Glasstone. The large acid weakening effects in *p*-cresol and *p*-fluorophenol, the less marked weakening in the other *p*-halogenophenols and the large acid strengthening in *p*-nitrophenol are clearly shown just as for the comparable treatment of the benzoic acids and as for the more quantitative treatment by the Sarmousakis method. There is further a marked acid weakening effect in *o*-chloro-, *o*-bromo- and *o*-iodophenol. This effect is distinctly different from the resonance effect in the *p*-halogenophenol which is small except for the fluorophenol. There is also an acid weakening effect in *o*-nitrophenol shown and, in the case of *o*-cresol, there is an acid strengthening which at least compensates for the acid weakening resonance which appears in *p*-cresol.

The theoretical weakness of the treatment based on the field strength at the number one carbon atom is recognized. The basis for suggesting the further use of this treatment for the study of deviations from the normal inductive effects is that the effects indicated by this treatment for the phenols and benzoic acids can all be accounted for in terms of resonance forms which are reasonable in the light of our present knowledge.[19] Except for the effects in *o*-halogenophenols and in *o*-nitrobenzoic acid, these deviations from the inductive effect have been previously accepted. The effect in *o*-nitrobenzoic

acid is small and therefore not definitely established. The effect in the *o*-halogenophenols is clearly established if this method of treatment is valid.

Summary

The Sarmousakis modification of the Kirkwood–Westheimer method of calculating the ratio of the dissocation constant of a substituted acid to that of the unsubstituted acid has been used to calculate values for the meta- and parasubstituted phenols and benzoic acids. Using a consistent set of assumptions it has been possible to adjust the parameters so that agreement could be obtained between the calculated and the observed values for aqueous solutions for both the meta-substituted phenols and the metasubstituted benzoic acids. The differences between the calculated and observed values for the parasubstituted acids have been calculated as a measure of resonance effects.

Following a suggestion made by Jenkins, values of $\log K_{A_xB_6}/F$ were calculated relating the ratio between the dissociation constants to the field strength at the ring carbon atom due to the dipole. Differences in this ratio for the corresponding ortho-, meta- and parasubstituted acids have been interpreted qualitatively in terms of resonance and chelation effects.

STAMFORD, CONN.
CHICAGO, ILL.

Preparation and Polymerization of Unsaturated Quaternary Ammonium Compounds[1,2]

BY GEORGE B. BUTLER AND ROBERT L. BUNCH

The absence of information in the literature concerning the polymerization of unsaturated quaternary ammonium compounds prompted us to study the preparation and polymerization of compounds of this type as a possible source of water insoluble polymers containing strongly basic groups. Products of this nature should be capable of absorbing negative ions from neutral salt solutions.

Since the presence of nitrogen in organic compounds quite often exhibits an inhibitory effect on peroxide catalyzed polymerization, there was some doubt that polymerization of these compounds could be accomplished. However, since quaternary ammonium halides are salts of strong bases and strong acids, it appeared likely that

polymerization of these neutral salts would occur under the proper conditions. This was found to be the case as described in detail below.

In order for a cross-linked polymer to result from vinyl type polymerization of a pure unsaturated quaternary ammonium salt, the presence of at least two unsaturated groups in the molecule is essential. Therefore, all of the compounds studied have contained at least two unsaturated groups, while some have contained three or four. The compounds were prepared by reaction of unsaturated tertiary amines, several of which had not been prepared previously with the appropriate alkyl halides. The majority of the compounds were prepared as the bromides, and were found to have rather high melting points. Introduction, however, of relatively high molecular weight radicals such as benzyl usually lowered the melting point. Most of the salts were found to be rather hygroscopic and are very soluble in water, low molecular weight alcohols, and formamide, fairly soluble in hot ketones, but insoluble in most other organic solvents.

TABLE I
UNSATURATED TERTIARY AMINES

| Compound	Formula	B. p. °C.	Mm.	d^{25}_{25}	n^{25}D	Nitrogen analyses, % Calcd.	Found	Yield, %
N-Allylmorpholine[a]	$C_7H_{13}NO$	156–8	768	0.9267	1.4569	11.02	10.98	60
N,N'-Diallylpiperazine[b]	$C_{10}H_{18}N_2$	213	761	.8865	1.4761	16.88	16.80	31
Diallylbenzylamine[c]	$C_{13}H_{17}N$	89	4	.9109	1.5122	7.48	7.39	73
N-β-Methylallylpiperidine	$C_9H_{17}N$	165	760	.8351	1.4559	10.06	9.88	42
N-β-Methylallylmorpholine	$C_8H_{15}NO$	171	760	.9120	1.4555	9.91	9.74	61
Diallylbutylamine[d]	$C_{10}H_{19}N$	170	760	.7863	1.4389	9.14	9.11	53
N,N'-Di-β-methylallylpiperazine	$C_{12}H_{22}N_2$	235	760	.8692	1.4710	14.42	14.11	52

[a] Picrate, m. p. 118°; chloroplatinate, m. p., 183.5°; picrolonate, m. p. 213°. N-Allylmorpholine was prepared by (1) reaction of morpholine and allyl bromide and (2) reaction of allylamine and β,β'-dichloroethyl ether. [b] Picrate, m. p. 254° (d); chloroplatinate, m. p. 280°. [c] Prepared from organic halide and diallylamine. [d] Previously reported without physical constants Brauchli and Cloetta [Chem. Zentr., 99, I, 2732 (1928)].

The high melting points of these compounds made it necessary to attempt polymerization either in solution, or by addition of some component to lower the melting points. Their solubility in water suggested the use of water soluble catalysts such as hydrogen peroxide, ammonium or potassium persulfate. However, attempts to obtain polymerization of aqueous solutions of these compounds using these catalysts were unsuccessful. Attempted polymerizations using benzoyl peroxide and di-t-butyl peroxide as catalysts were also unsuccessful.

Addition of suitable components for lowering the melting point to a desirable range proved to be quite valuable in some cases. Equal quantities of triallylbenzylammonium bromide, which melts at 132°, and several of the higher melting compounds when thoroughly mixed resulted in solids which fused to clear liquids in the range of 85–95°. Addition of a small quantity of t-butyl hydroperoxide to these fused masses resulted in copolymerization of the mixture.

Further polymerization studies revealed the fact that fusion temperatures of these compounds could be lowered tremendously by the addition of extremely small amounts of water or formamide. Examples illustrating these methods of polymerization are given under the experimental section.

The polymers and copolymers of these compounds have been found to undergo the ion exchange reactions as predicted. The complete cycle is illustrated in the following series of reactions

$$nR_4NBr \xrightarrow[\text{hydroperoxide}]{t\text{-Butyl}} (R_4NBr)_n$$
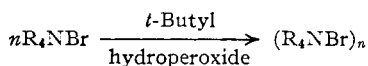
(R groups may be equal or different. At least two groups are unsaturated.)   Cross-linked, water insoluble polymer. (Washed free of soluble bromides.)

$$(R_4NBr)_n + nKOH \longrightarrow (R_4NOH)_n + nKBr$$
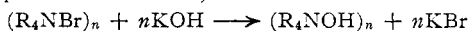
Continued until no halogen present in filtrate. Resin washed until neutral filtrate obtained.

$$(R_4NOH)_n + nKCl \longrightarrow (R_4NCl)_n + nKOH$$
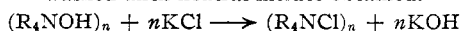
Filtrate was very strongly basic.

Experimental

Materials.—Piperazine hexahydrate and piperidine (practical grade) were obtained from Eastman Kodak Company and used as received. The n-butylamine and

morpholine were obtained from Carbide and Carbon Chemical Company and used without further treatment. The diallylamine, allyl chloride, β-methylallyl chloride, and di-t-butyl peroxide were obtained through the courtesy of Shell Chemical Company. The allyl chloride and β-methylallyl chloride were redistilled before use. The allyl bromide was obtained from Dow Chemical Company and used without further purification. The t-butyl hydroperoxide was obtained as a 60% solution through the courtesy of Union Bay State Company.

Preparation of Unsaturated Tertiary Amines.—The unsaturated tertiary amines required for this work were prepared by a modification of the procedure outlined in "Organic Syntheses"[3] for preparation of benzylaniline. The secondary amine was treated with a 0.05 mole excess of the appropriate halide in presence of a 0.25 mole excess of sodium bicarbonate in aqueous solution. The amines were purified by distillation after separation from the aqueous solution and drying.

Since the number of unsaturated tertiary amines recorded in the literature is surprisingly small, many of these are new compounds. The properties, analyses and yields of these new tertiary amines are summarized in Table I.

Preparation of Quaternary Ammonium Salts.—An equimolecular quantity of the appropriate alkyl or alkenyl halide was added dropwise, with stirring, to a hot solution of the unsaturated tertiary amine in acetophenone. Stirring was continued, and the solution was refluxed gently for approximately two hours. In most cases the products were insoluble in the solvent and crystallized on cooling. Purification was accomplished by recrystallization from ketones, alcohol–ether mixtures, or formamide–acetone mixtures. The products were stored under anhydrous conditions to prevent absorption of moisture. The properties, analyses, and yields of these compounds are summarized in Table II.

Polymerization Studies.—The following experiments will serve to illustrate the methods of polymerization and the ion-exchange properties of the polymers:

(1) One-half gram of triallylbenzylammonium bromide and 0.5 g. of tetraallylammonium bromide were mixed well and placed in a bath at 110°. Fusion of the mixture began at 85° and was complete at 95°, a clear solution being obtained. When the temperature of the liquid reached 108°, five drops of 60% t-butyl hydroperoxide was added with stirring, and the reaction vessel removed from the bath. Polymerization began immediately as was evidenced by a temperature rise to 140°. A rubbery mass having a reddish-brown color was formed. When the exothermic reaction was over, the vessel was returned to the bath and heating continued at 125° for two hours. The polymer was insoluble in water.

(2) Ten grams of tetraallylammonium bromide, 0.94 g. of formamide and 0.22 g. of 60% t-butyl hydroperoxide were mixed well and placed in an oven at 75°. Fusion was

(3) "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., p. 102.

TABLE II
UNSATURATED QUATERNARY AMMONIUM HALIDES

Bromide	Formula	Allyl bromide reacted with:	M. p., °C.	Bromine analyses, % Calcd.	Found	Yield, %
Ethyltriallylammonium	$C_{11}H_{20}BrN$	Ethyldiallylamine	159	32.47	32.65	77
Triallylbutylammonium	$C_{13}H_{24}BrN$	Diallylbutylamine	175	29.14	28.98	77
Diallylmorpholinium	$C_{10}H_{18}BrNO$	Allylmorpholine	213	32.21	32.30	89
Tetraallylpiperazinium di-	$C_{16}H_{28}Br_2N_2$	N,N'-Diallylpiperazine	207	39.25	39.26	67
Tetraallylammonium[a]	$C_{12}H_{20}BrN$	Triallylamine	185	30.95	31.07	69
Diallylpiperidinium	$C_{11}H_{20}BrN$	N-Allylpiperidine	190[b]	32.47	32.64	79
Triallylbenzylammonium	$C_{16}H_{22}BrN$	Diallylbenzylamine	132	25.93	25.70	71
Allyl-β-methylallylmorpholinium	$C_{11}H_{20}BrNO$	β-Methylallylmorpholine	197	30.48	30.56	53
Allyl-β-methylallylpiperidinium	$C_{12}H_{22}BrN$	β-Methylallylpiperidine	195.5	30.71	31.10	72
Diallyl di-β-methylallylpiperazinium di-	$C_{18}H_{32}Br_2N_2$	N,N'-Di-β-methylallylpiperazine	182	36.63	36.57	54
Di-β-methylallylpiperidinium	$C_{13}H_{24}BrN$	β-Methylallylpiperidine[c]	175	29.14	29.21	63
Diallylmorpholinium[d]	$C_{10}H_{18}ClNO$	Allylmorpholine	180	17.41	17.29	65

[a] Previously reported as decomposing at 80°, Grosheintz [Bull. soc. chim., [2] 31, 391 (1879)]. [b] This is a flash m. p.; no true melting point on slow heating. [c] β-Methylallyl bromide was the reacting halide in this case. [d] The compound prepared was the chloride. Allyl chloride was the reacting halide. The reported analytical values are % chlorine.

complete at this temperature. After a short time, the liquid became a dark brown, glassy solid. After twenty hours in the oven at 75°, the polymer was removed and washed with hot water, 7.6 g. of a granular, water insoluble substance being obtained.

(3) Ten grams of triallylbutylammonium bromide, 0.39 g. of distilled water and 0.11 g. of 60% t-butyl hydroperoxide were mixed well and placed in an oven at 100°. After twelve hours, the temperature was raised to 125° and held for twelve hours. The polymer was obtained in a 52.5% yield as a light brown, granular, water insoluble product.

(4) The copolymer obtained from triallylbenzylammonium bromide and tetraallylammonium bromide was washed with hot distilled water until the filtrate no longer gave a test for halogen. It was then treated with a 1% solution of potassium hydroxide, stirred at room temperature for several minutes and filtered. The filtrate, after acidifying with halogen-free nitric acid, gave a precipitate of silver bromide upon addition of silver nitrate, showing that the polyquaternary ammonium bromide was being converted to the polyquaternary ammonium hydroxide and releasing bromide ions. This treatment was continued until the acidified filtrate was found to be halogen-free, indicating that replacement of the halogen ion with hydroxyl ion was complete. This was shown to be correct by decomposing a sample of the dried polymer by sodium fusion and testing for halogen in the filtrate, no precipitate of silver bromide being formed. The product was washed with distilled water until a neutral filtrate was obtained.

Upon treatment of the polymer with a neutral solution of potassium chloride, a strongly basic filtrate was obtained, showing that chloride ions were removed from solution by the polymer, and hydroxide ions released.

Acknowledgment.—We are indebted to Mr. A. E. Potter, Mr. J. L. Wester and Mr. R. L. Goette of this Laboratory for many of the analyses reported here, as well as for additional valuable assistance.

Summary

Several new unsaturated tertiary amines and quaternary ammonium salts have been prepared and characterized.

These unsaturated quaternary ammonium halides have been polymerized to water insoluble polymers, and it has been shown that these polymers may be converted to the polyquaternary ammonium hydroxides by an ion exchange reaction with potassium hydroxide resulting in the formation of a series of strongly basic ion exchange resins.