Committee could easily be determined with high precision. The content of silicic acid in water for a high-pressure boiler of a thermal power generator was maintained at a constant level during circulation in the plant.

In the case of the gel-phase colorimetry, concentration of the molybdenum blue species and the color development take place simultaneously. As a result, silicic acid at parts-per-billion or lower levels can be determined in a conveniently short time. Within 90 min, six samples could be analyzed.

Registry No. Silicic acid, 7699-41-4; water, 7732-18-5.

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Spectrophotometric Determination of Amines with *p*-Chloranil

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Primary, secondary, and tertiary amines, both aliphatic and aromatic are shown to react with *p*-chloranil in dioxane/2-propanol (1:4, v/v) to produce a blue to purple color. Most amines tested also react with *p*-chloranil in other organic solvents. The colored compound formed can be stable for 8 h at room temperature, depending on the amine and the solvent used. Several organic compounds (phenol, epoxies, alkynes, and non-amine nitrogens) are shown to not interfere with the determination of amines. A few applications of amine determinations in real samples are discussed. The reaction product is identified as monoamine quinones where the amine displaces one chlorine of the *p*-chloranil. Tertiary amines react to form water-soluble, surface active quatenary amines. Detection limits vary with each amine, but for *N,N,N',N'*-tetramethylethylenediamine, the detection limit is 0.05 mg.

A method was required to determine tertiary amine catalysts used in the synthesis of alkynes. Ideally, the method would be rapid and reproducible and require little or no instrumentation. Hopefully, a solution of the alkyne being synthesized could be added to a test solution. If a tertiary amine were present, the test reagent would turn a bright color.

A test reagent which has been shown to react with a variety of amines is *p*-chloranil (i.e., 2,3,5,6-tetrachlorobenzoquinone). Sass et al. (*1*) described the formation of a green color when tertiary amines in toluene reacted with *p*-chloranil on a boiling water bath. More recently, Ibrahim et al. (*2*) described the formation of a blue color when certain tertiary amine type tranquilizers and antidepressants reacted with *p*-chloranil in a dioxane–ethanol mixture (1:4, v/v). The tertiary amines that they studied did not react with *p*-chloranil in toluene. Taha and El-Kader (*3*) described the use of *p*-chloranil as a spray reagent for tertiary *N*-ethyl drugs on thin-layer chromatograms. Other workers have reported reactions between tertiary amines and *p*-chloranil in a variety of solvents (*4–10*). Some of these reports, as well as others (*11–19*) have shown that a number of primary and secondary, aliphatic and aromatic amines also react with *p*-chloranil. Again, a variety of solvents and reaction conditions were used in these studies.

The present work was performed to better characterize the use of *p*-chloranil as a spectrophotometric reagent for the determination of amines. It is demonstrated that *p*-chloranil does react with a variety of amines in a dioxane–2-propanol mixture (1:4, v/v) to produce a blue or purple color. This method is shown to be ideal for a quick spot test in monitoring the purity of alkynes.

The effects of solvent on the reaction of amines with *p*-chloranil and upon the stability of the colored complexes are also reported. A few applications for the determination of amines are discussed. The reactions involved in developing the purple color are identified.

EXPERIMENTAL SECTION

Ultraviolet (UV) and visible spectra were measured with a Perkin-Elmer Model 320 spectrophotometer. Infrared spectra were recorded with a Nicolet Model 7199 Fourier transform infrared (FTIR) spectrometer operating at 2 cm^{-1} resolution. Nuclear magnetic resonance (NMR) spectra were obtained with a Varian FT80A NMR at either 79.542 MHz (^1H NMR) or 20.000 MHz (^{13}C NMR). Amines were determined by adding 2 mL of a 0.5% solution of *p*-chloranil in 1,4-dioxane to 8 mL of amine in 2-propanol at room temperature. After an appropriate time (see Table I), the absorbance at the optimum wavelength in the visible region (λ_{max}) was measured.

Synthesis and Purification of Amine–Quinones. *Isobutylamine- and Morpholine–Quinones.* To 40 mg (0.16 mmol) of *p*-chloranil in 8 mL of dioxane, either 6.4 mg (0.09 mmol) of isobutylamine or 8.2 mg (0.09 mmol) of morpholine in 32 mL of CH_2Cl_2 was added. The mixtures were stirred for 1 h at room temperature and transferred to a rotoevaporator to remove the solvent under vacuum. The residues were redissolved in CH_2Cl_2 and applied to a preparative scale silica TLC plate. The plates were developed in CH_2Cl_2. In each case, a dark purple band was separated and scraped into a 50-mL beaker. The purple compounds were redissolved in CH_2Cl_2. The CH_2Cl_2 was evaporated under a stream of nitrogen and some of the purple solid was pressed into a KBr pellet for IR analysis. Some of the morpholine–quinone was redissolved in acetone-d_6 for NMR analysis.

Tributylamine- and Tetramethylethylenediamine–Quinones. To 40 mg of *p*-chloranil in dioxane, either 29 mg (0.16 mmol) of tributylamine or 20 mg (0.16 mmol) of tetramethylethylenediamine in 32 mL of 2-propanol was added. The solvent was stirred for 30 min at room temperature and removed by rotoevaporation in vacuo. The residues were redissolved in 2-propanol and applied

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Table I. Reactions with 40 μmol of Chloranil[a]

compound	amine, μmol	λ_{max}	absorbance	reaction time, min
imidazole	7.84	538–542	0.195	45
m-toluidine	7.92	545–555	0.540	120
p-toluidine	6.74	545–555	0.570	75
1,3-di-*o*-tolylguanidine	7.40	540–545	0.290	7
4,4′-diaminodiphenylmethane	9.76	558–562	0.740	30
N-methylmorpholine	7.76	540–545	0.201	75
triethanolamine	7.65	541–547	0.370	90
diethanolamine	7.24	545–555	0.331	15
ethanolamine	7.80	540–550	0.325	13
morpholine	7.71	543–547	0.69	14
tetramethylethylenediamine	7.63	551–555	0.54	30
dimethylethylenediamine	8.24	500–510	0.57	24
ethylenediamine	7.21	491–495	0.61	24
cyclohexylamine	7.35	535–545	0.266	7
2-ethylhexylamine	8.10	535–540	0.256	9
tri-*n*-butylamine	6.41	540–546	0.35	15
di-*n*-butylamine	7.84	545–550	0.40	6
isobutylamine	7.04	540–545	0.242	8
dicyclohexylamine	7.15	539–542	0.275	12
pyrrolidine	7.88	554–556	0.524	4
piperidine	7.77	561–563	0.592	7
hexamethylenetetramine	8.49	538–542	0.248	180

[a] These reactions were run at room temperature in 80% 2-propanol/20% 1,4-dioxane.

to a preparative scale silica TLC plate. The plates were developed in 2-propanol and the dark purple bands were separated and scraped into a beaker. Each sample was redissolved in acetone, and the acetone was evaporated under a stream of nitrogen.

RESULTS

Amines Which React with *p*-Chloranil. Chloranil reacts with a variety of primary, secondary and tertiary, aliphatic, and aromatic amines at room temperature in a dioxane–ethanol (1:4, v/v) mixture. In the first set of experiments, the reaction was allowed to proceed until the color intensity seemed to be constant. The visible absorbance spectrum was then recorded. For all the compounds listed in Table I, a broad peak was observed. For most compounds (those with λ_{max} from 540 to 560) the solution was blue or purple. In the second set of experiments, the wavelength of the spectrophotometer was set at the λ_{max} determined in the first set of experiments. To 8 mL of amine in 2-propanol, 2 mL of 20 mM *p*-chloranil in dioxane was added. The sample was mixed and put into the spectrophotometer where the increase in absorbance with time was observed.

The results from three such rate studies are shown in Figure 1. The time required to reach miximum absorbance is shown in Table I for each amine. 1,3-Di-*o*-tolylguanidine reacts under these conditions to form this same blue-purple color.

HCl salts of amines do not react with *p*-chloranil. In fact, adding HCl to the purple solutions will turn them light yellow (the color of unreacted *p*-chloranil). The procedure of neutralizing an amine–HCl with NaOH or Na_2CO_3 should not be used because NaOH itself reacts with *p*-chloranil to form a blue compound (*20*). To determine amine–HCl, it is necessary to first neutralize the HCl and then extract the amine into a nonaqueous solvent. Ibrahim et al. (*2*) suggested extracting the neutralized amine into $CHCl_3$ and then evaporating the $CHCl_3$.

Stability of Reaction Product. The blue-purple colored product formed when tetramethylethylenediamine (TMED) reacts with *p*-chloranil in 2-propanol/dioxane is quite stable for 8 h; however, when the reaction was run in ethanol, the absorbance at 553 nm decreased 20% in 8 h. When the reaction was run in methanol, the absorbance at 553 nm decreased 45% in 8 h.

The blue-purple colored product formed when other amines reacted with *p*-chloranil in 2-propanol/dioxane was not always

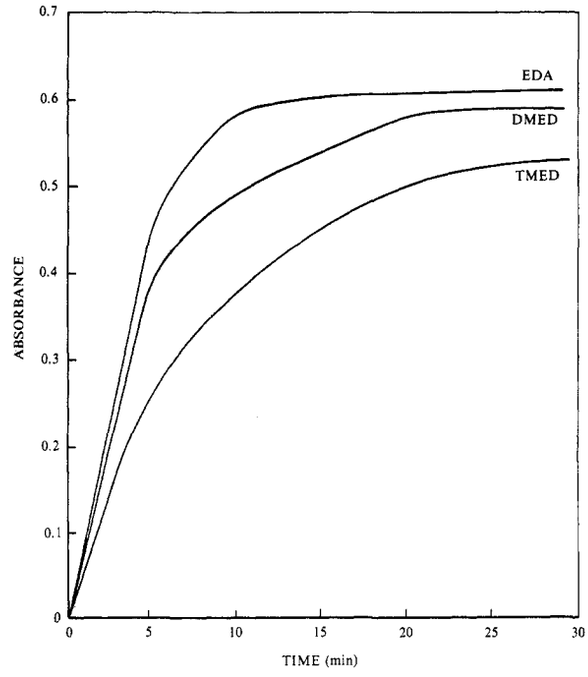


Figure 1. Reaction between 2.0 mM *p*-chloranil and 0.721 mM ethylenediamine (EDA), 0.824 mM *sym*-dimethylethylenediamine (DMED), and 0.763 mM *N*,*N*,*N*′,*N*′-tetramethylenediamine (TMED).

Table II. Stabilities of Reaction Products in 1-Propanol

amine	% decrease in abs after 2 h[a]
ethanolamine	43
diethanolamine	39
triethanolamine	8
isobutylamine	41
dibutylamine	38
tributylamine	31
morpholine	16
tetramethylethylenediamine	2
cyclohexylamine	60
dicyclohexylamine	49

[a] The wavelengths at which the absorbances were measured are those listed in Table I.

Table III. Effect of Solvents on Reactions with 40 μmol of *p*-Chloranil

solvent	λ_{max}	abs	reaction time, min
Reaction with 17.6 μmol of Isobutylamine			
dioxane	525–530	0.318	45
THF	530	0.472	8
acetonitrile	545–555	0.665	8
dichloromethane	535–540	0.538	30
chloroform	535–540	0.478	45
1-propanol	540–545	0.703	8
acetone	500–510[a]	0.195[a]	10
Reaction with 25.7 μmol of Morpholine			
dioxane	545–555	1.711	60
THF	545–555	2.093	6
acetonitrile	550–555	2.082	6
dichloromethane	560	2.782	20
chloroform	555–560	2.551	30
1-propanol	543–547	2.301	14
acetone	565	2.389	6
Reaction with 6.4 μmol of tri-*n*-butylamine			
Dioxane	530–540	0.129	90
THF	540–550	0.225	90
Acetonitrile	550–555	0.315	8
Dichloromethane	545–555	0.238	45
Chloroform	545–555	0.203	60
1-propanol	545–550	0.334	15
Acetone	550	0.311	10

[a] The reaction in acetone produced an additional peak at 387 nm.

stable. The stabilities of some of the amine–*p*-chloranil purple reaction products for 2 h are shown in Table II.

Morpholine reacts with *p*-chloranil in dioxane/2-propanol within 14 min (Table I) to give an intense blue-purple color. Two hours later, the absorbance at 545 nm decreases 16%. However, in dichloromethane/dioxane (4:1, v/v), morpholine reacts with *p*-chloranil within 20 min, but the absorbance at 560 nm is stable for at least 2 h.

Reactions in Different Solvents. To further test this solvent effect, isobutylamine, morpholine, and tri-*n*-butylamine solutions were prepared in 8 mL of seven different solvents. To these solutions 2 mL of 20 mM *p*-chloranil was added. The times required to reach maximum absorbances, along with λ_{max} and absorbance values, are listed in Table III. Thus, it is possible to vary the solvent used to determine a given amine, or combination of amines. For example, the tertiary amine tetramethylethylenediamine (TMED) is a catalyst used in the synthesis of 1,1′-(1,3-butadiyne-1,4-diyl)bis(cyclopentanol) (DCPB). The DCPB is readily soluble in ethanol (over 100 mg can be dissolved in 1 mL of ethanol). As little as 0.05 mg of TMED can be detected using the *p*-chloranil—thus providing a quick, easy test for purity of the DCPB. A tertiary amine used in an epoxy resin also can be determined. One such epoxy resin contains the tetraglycidyl ether of 4,4′-diaminodiphenylmethane (TGDDM). TGDDM is not readily soluble in 2-propanol; however, it is quite soluble in acetone. TGDDM does react at room temperature with *p*-chloranil in an acetone/dioxane (4:1, v/v) solution to produce a blue-green (turquoise) color. The λ_{max} is at 614 nm, and the absorbance when 10 μmol are taken (in 10 mL total volume) is 0.606 after 60 min. Thus, it is quite possible to alter the solvent conditions to optimize the determination of an amine in the desired matrix.

Nitrogen Compounds Which Do Not React. Not all amines react at room temperature with *p*-chloranil. Triphenylamine, diaminodiphenyl sulfone, pyridine, 2-aminopyridine, *o*-toluidine, and carbazole do not react in the 2-propanol/dioxane solution at room temperature. Pyridine does react slowly at 60 °C. After 2 h, the solution turns orange. The λ_{max} is at 460 nm and the absorbance was 1.6. None of the other amines were tested for reaction with *p*-chloranil either at elevated temperature or in more polar solvents.

In addition, not all nitrogen compounds react with *p*-chloranil in 2-propanol/dioxane. Those tested which did not react include triphenylamine, pyridine, diaminodiphenyl sulfone, *o*-toluidine, indole-2,3-dione, acetonitrile, caprolactam, ethyl carbamate, azobenzene, carbazole, benzimidazole, 1,1-dimethylhydrazine, and 2-aminopyridine.

Table IV. Applications

amt of sample, mg	sample	amine added, mg	amine found, mg
108.3	dicyclopentanolbutadiyne	0.222[a]	0.226
323.5	1-ethynylcyclopentanol	1.04[b]	1.08
19.5	*n*-butyl glycidyl ether	3.9[c]	4.0
23.9	phenyl glycidyl ether	3.9[c]	3.9
17	diglycidyl ether of bisphenol A	5.2[d]	5.2
65	phenol	2.5[e]	3.2

[a] Tetramethylethylenediamine added. [b] Ethylenediamine added. [c] 4,4′-diaminodiphenylmethane added. [d] Tetraglycidyl ether of 4,4′-diaminodiphenylmethane (TGDDM) added. [e] Hexamethylenetetramine added.

Applications. Several applications of amine determinations were investigated. The use of TMED in the synthesis of DCPB was previously discussed. The primary amine, ethylenediamine, is used as a catalyst in the synthesis of 1-ethynylcyclohexanol. Of this compound, 323.5 mg contained 0.06 mg of the ethylenediamine. The amine cure agent 4,4′-diaminodiphenylmethane can be determined in epoxy resins. Each of these amines was added to the substances of interest and were accurately determined as shown in Table IV. Not all amines can be determined so readily. Hexamethylenetetramine (sometimes referred to as methenamine) is used in preparing phenolic resins. Hexamethylenetetramine does react with *p*-chloranil, but the purple color is not as intense as those seen with other amine reactions. In the presence of excess phenol, the purple color is more intense. Phenol itself does not react with *p*-chloranil. Perhaps there is an equilibrium between the reaction product and the unreacted *p*-chloranil plus hexamethylenetetramine. (Similar to the equilibrium proposed by Foster (*16*) in the reaction between *p*-chloranil and tetramethylphenylenediamine). Perhaps phenol shifts this equilibrium to a more complex formation. Similarly, if 5.2 mg of TGDDM is mixed with 103 mg of diglycidyl ether of bisphenol A (DGEBA), only 4.5 mg of TGDDM is found. Thus, an excess of DGEBA can shift the equilibrium to unreacted amine and *p*-chloranil.

Identification of Reaction Products. *Isobutylamine–Quinone.* The purple isobutylamine–quinone product was not soluble in water, but was soluble in several organic solvents. The infrared spectrum did not have the NH_2 deformation band which appears at 1640 cm^{-1} in unreacted isobutylamine.

Morpholine–Quinone. The morpholine–quinone product was not soluble in water but was soluble in organic solvents. The infrared spectrum did not have the N–H stretch band which occurs in the 3300-cm^{-1} region in unreacted morpholine.

This purple reaction product was highly soluble in acetone-d_6 so that a ^{13}C NMR spectrum could be acquired. Unreacted morpholine has two peaks—at 68.48 (for the $-CH_2-O-CH_2-$ carbons) 47.25 ppm (for the $-CH_2-N-CH_2-$ carbons). Unreacted *p*-chloranil has two peaks—at 140.84 (C=C carbons) and at 170.00 ppm (C=O carbons). Because of molecular symmetry, only two peaks are expected for the *p*-chloranil. The morpholine–*p*-chloranil reaction product had

eight peaks—at 67.96 ($-CH_2-O-CH_2-$), 52.65 ($-CH_2-N-CH_2-$); at 149.19, 141.06, 138.91, and 118.69 for the C=C carbons; and at 175.29 and 171.75 for the C=O carbons. The ^1H NMR spectrum of the morpholine–*p*-chloranil reaction product in CD_2Cl_2 had two triplets at 3.79 and 3.57 ppm. Unreacted morpholine has triplets at 3.53 and 2.73 ppm.

Tertiary Amine–Quinones. The tri-*n*-butylamine and the TMED–quinones both were very soluble in water. The solutions foamed easily when agitated. The ^1H NMR spectrum of the TMED–quinone had singlets at 4.15, 2.94, and 2.57 ppm in about a 6:4:6 ratio (peak areas). The unreacted TMED had only two singlets—at 2.20 and 2.42 ppm in about a 12:4 ratio.

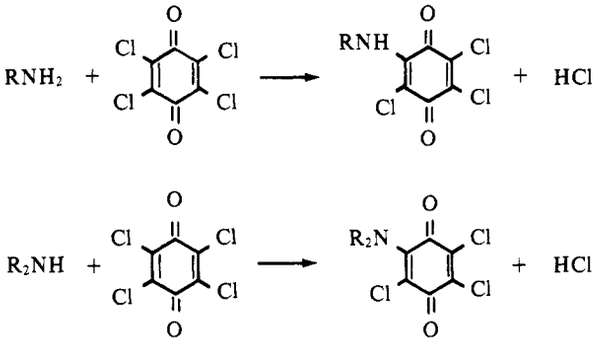
DISCUSSION

Comparison with Other Reagents. Fluorescamine and *o*-phthalaldehyde are well-known reagents for the fluorescence determination of amino acids (*21*, *22*). However, as with *p*-chloranil, neither of these reagents can be used to determine tertiary amines, and neither are suited for determining amines in nonaqueous solvents. Both fluorescamine and *o*-phthalaldehyde were recommended along with Ehrlich's reagent (*23*) (*p*-dimethylaminobenzaldehyde), ethyl Ehrlich's reagent (*24*), *p*-dimethylaminocinnamaldehyde (*23*, *25*), and *p*-chloranil as possible reagents for detecting small amounts of primary amines on solid surfaces (*26*). In addition, H-acid (9-amino-1-hydroxynaphthalene-3,6-disulfonic acid) and N-na (*N*-[1-naphthalenyl)-1,2-ethanediamine) are useful colorimetric reagents for determining a variety of primary and secondary amines (*27*). However, neither of these reagents were suited for determining phenylenediamines. The phenylenediamines (ortho, meta, and para isomers) were tested for their reactivity with *p*-chloranil and 2-propanol/dioxane (4:1, v/v). Each isomer produced a different color immediately when mixed with *p*-chloranil, and each color faded rapidly. Eight micromoles of *m*-phenylenediamine (in 8 mL of 2-propanol) turn red when mixed with *p*-chloranil and a shoulder from 440 to 480 nm was observed on a much larger peak in the UV region. (Unreacted *p*-chloranil has a UV absorbance and undoubtedly reaction products would also have a UV absorbance.) This red color faded within 5 min. Eight micromoles of *p*-phenylenediamine (in 8 mL of 2-propanol) turned green and two peaks, at 468 and 497 nm, were seen in the visible region immediately after adding the 2 mL of *p*-chloranil. Again, the green color faded and was probably not suited for quantitation. Seven micromoles of *o*-phenylenediamine turned brown, and a peak from 640 to 660 nm was seen in the visible spectrum immediately upon additive of *p*-chloranil. The absorbance decreased and a new peak, at 450 nm, appeared and increased steadily for 1 h. Thus, *p*-chloranil is similar to H-acid and N-na in that it can be used to determine several aromatic amines, but quantitation of phenylenediamines is either difficult (with *p*-chloranil) or impossible (with H-acid and N-na).

Use as a Reagent in Chromatography. The reagent *p*-chloranil is also ideally suited to be a spray reagent to identify amines by thin-layer chromatography (TLC). Previous workers have reported its use in visualizing amines after normal phase TLC with silica plates (*3*). If NH_4OH is used in the developing solution (as was done by Taha and El-Kader (*3*)), it is important to allow all the ammonia to evaporate off the plate completely before spraying the plate. Otherwise, the NH_4OH still on the plate will react with the *p*-chloranil to cover the plate with a blue background. A 0.1% solution of *p*-chloranil in ethanol spray reagent has been successfully used in the Bendix lab to spray both normal phase silica and reverse phase C-12 plates. Other spray reagents were reported for visualizing amines after TLC, but most of these will not react with tertiary amines. One reagent, 2-naphthyl chloroformate, reportedly reacts with tertiary amines, but it is synthesized from 2-naphthylamine, a known carcinogen (*28*, *29*). Similarly, it is posible that *p*-choranil could be used for precolumn derivatization of amines for selective detection by liquid chromatography. A number of similar reagents have also been reported. These include acid chlorides (*30*), fluorescamine (*31*), dansyl chloride (*32*), 4-chloro-7-nitrobenzo-2,1,3-oxadiazole (*33*), 2,4-dinitrofluorobenzene (*34*), and iodine (*35*).

Advantages of *p*-Chloranil. The reagent *p*-chloranil can be used for determining primary and secondary, aliphatic, and aromatic amines. However, *p*-chloranil is particularly useful in determining tertiary amines. It is also quite useful in determining amines in hydrophobic systems and is ideally suited for a quick spot test for amines during organic synthesis (of alkynes) or for analyzing unknown organics. Bases such as NaOH, NH_4OH, and Na_2CO_3 give a "false positive" test for amines.

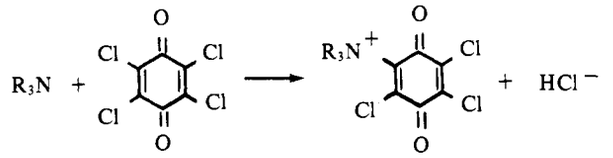
Reactions Involved in Color Development. Buckley and others (*36*) synthesized two monosubstituted amino–quinones by reacting either dimethylamine or morpholine with a molar excess of *p*-chloranil. They isolated the reaction products and found their elemental composition to be consistent with the production of a monosubstituted product. The UV–visible spectra of these products are very similar to the UV–visible spectra of the isobutylamine and morpholine–quinones prepared in this study (absorbance at 550 and 300 nm). Thus, the following reactions are proposed:



The infrared data reported in this study are consistent with these proposed reactions. When the primary amine, isobutylamine, reacts with *p*-chloranil, the NH_2 band at 1640 cm^{-1} disappears. When the secondary amine, morpholine, reacts with *p*-chloranil, the N–H stretch at 3300 cm^{-1} disappears. In addition, one reaction was run between 0.16 mmol of *p*-chloranil and 0.08 mmol of morpholine in CH_2Cl_2 with no dioxane present. After 1 h, the reaction mixture was extracted with water and the water extract was analyzed by ion chromatography (see ref 37 and 38 for experimental details used in ion chromatography). Results showed that 0.076 mmol of HCl had been extracted into the aqueous phase, thus establishing that HCl is truly a reaction product.

The ^{13}C NMR data also support the proposed reaction. The only way that four phenyl (C=C) and two carbonyl carbons can be unique is for the morpholine to displace one and only one chlorine on the *p*-chloranil. If morpholine were to form a Schiff base (C=N) as proposed by Kreingold et al. (*4*) molecular symmetry would indicate that there be four different carbons (two phenyl and two carbonyl). Similarly, if more than one chlorine were displaced to give a di-, tri-, or tetraaminoquinone, molecular symmetry would again cause less than six different carbons (excluding the CH_2-N-CH_2 and CH_2-O-CH_2 from morpholine). When the molar ratio of morpholine to *p*-chloranil exceeds 1:1.5, the diaminoquinone can be produced. However, the UV–visible spectrum is quite different from that of the monoamine with peaks near 435 and 240 nm (*36*). The UV–visible spectrum of the morpholine reacted with a 2-fold molar excess of *p*-chloranil does not

exhibit the peaks at 435 and 240 nm. For the reaction between tertiary amines, a quatenary amine is produced, as suggested by Sass and others (*1*) and by Shah and Murthy (*9*)



The strongest evidence for this reaction is that the TMED–*p*-chloranil and the tributylamine–*p*-chloranil are both readily soluble in water and both act as surfactants. The ^{1}H NMR data also support the proposed reaction. Before reacting, the four methyl groups of TMED are equivalent with a chemical shift of 2.20 ppm. After reacting with *p*-chloranil, the two pairs of methyl groups became nonequivalent. The methyl protons closest to the quinone ring are shifted furthest downfield (to 4.15 ppm). The other set of methyl protons are shifted only slightly (to 2.57 ppm). Similarly, the methylene protons are shifted downfield from 2.42 to 2.94 ppm. This downfield shift of proton chemical shifts is similar to that seen in the morpholine–*p*-chloranil reaction product.

One final experiment was performed to ensure that TMED reacts with *p*-chloranil to form a monoaminoquinone. The mole ratio of TMED to *p*-chloranil was varied from 0.1 to 10.0 and the absorbance at 550 nm recorded. By this method of Job (*39*), it was found that maximum absorbance occurred when the TMED to *p*-chloranil ratio was 1:1, indicating that the monoaminoquinone was formed. Even at the extremes, when TMED to *p*-chloranil was 0.1 or 10.0, no new bands (like the 435-nm band in disubstituted morpholine–*p*-chloranil) were seen in the UV–visible spectrum.

OTHER REACTIONS

It is proposed that when the amines listed in Table I react with a 2-fold molar excess of *p*-chloranil that a monoamine-substituted quinone is produced. In the case of tertiary amines, a quatenary amine is produced. However, when *o*-, *m*-, or *p*-phenylenediamines react with *p*-chloranil, different colors and reaction products are formed. Some of these reactions were investigated by Nogami and others (*13*, *14*). They showed that *o*-phenylenediamine reacts with *p*-chloranil in ether to form a mixture of 2,3-diaminophenazine (yellow), *o*,*o*′-diaminoazobenzene (red), and tetrachlorohydroquinone (colorless). When *m*-phenylenediamine is the reactant, 2,5-dichloro-3,6-di-*m*-aminoanilino-*p*-benzoquinone is formed (*14*). Similarly, if other amines are present in a 1000-fold molar excess over the *p*-chloranil, disubstituted aminoquinones are formed (*10*, *15*).

CONCLUSIONS

Primary, secondary, and tertiary amines, including aliphatic and some aromatic amines react with *p*-chloranil in dioxane/2-propanol (1:4, v/v) to produce a blue or purple color. Neither phenols, epoxies, alkynes, or a variety of other non-amine nitrogens interfere with this reaction. Substituted guanidines, however, do seem to react. Strong bases such as NaOH and Na_2CO_3 also react with *p*-chloranil to give a blue color. HCl and HCl salts of amines do not react with *p*-chloranil. Thus, free amines in phenolic or epoxy resins, in partially purified alkynes, and in a number of other organic mixtures can be determined by using the colorimetric reagent *p*-chloranil. The blue color producing reaction involves the amine displacing one chlorine from the *p*-chloranil. However, some aromatic amines may react to give different colored products.

Registry No. TMED, 110-18-9; DMED, 110-70-3; EDA, 107-15-3; TGDDM, 92013-90-6; DCPB, 7179-09-1; DGEPA, 1675-54-3; isobutylamine–quinone, 92013-91-7; morpholine–quinone, 92013-92-8; tributylamine–quinone, 92013-93-9; TMED–quinone, 92013-94-0; *p*-chloranil, 118-75-2; imidazole, 288-32-4; *m*-toluidine, 108-44-1; *p*-toluidine, 106-49-0; 1,3-di-*o*-tolylguanidine, 97-39-2; 4,4′-diaminodiphenylmethane, 101-77-9; *N*-methylmorpholine, 109-02-4; triethanolamine, 102-71-6; diethanolamine, 111-42-2; ethanolamine, 141-43-5; morpholine, 110-91-8; cyclohexylamine, 108-91-8; 2-ethylhexylamine, 104-75-6; tri-*n*-butylamine, 102-82-9; di-*n*-butylamine, 111-92-2; isobutylamine, 78-81-9; dicyclohexylamine, 101-83-7; pyrrolidine, 123-75-1; piperidine, 110-89-4; hexamethylenetetramine, 100-97-0; 1-ethynylcyclopentanol, 17356-19-3; *n*-butyl glycidyl ether, 2426-08-6; phenyl glycidyl ether, 122-60-1; phenol, 108-95-2.

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