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Effects of Tetra-*n*-alkylammonium Ions on the Polarographic Reduction of Methyl *p*-Chlorophenylpropionate¹

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Tetra-*n*-alkylammonium ions are adsorbed onto the surface of a dropping mercury electrode over a wide range of potentials in 25% (v./v.) ethanol-water media. This adsorption results in pronounced changes in the half-wave potentials and diffusion currents of the polarographic waves obtained with methyl *p*-chlorophenylpropionate and also in the mechanism of the reduction. The effects depend upon both the size and the concentration of the tetraalkylammonium ion. They raise serious doubts of the validity of the common practice of employing salts of these ions as supporting electrolytes in explorations of the electrochemical properties of organic compounds by polarographic techniques.

Introduction

Relatively few studies of the polarographic behaviors of acetylenic compounds have been described in the literature. Laitinen and Wawzonek² observed that in 0.175 *F* tetra-*n*-butylammonium iodide-75% dioxane acetylenic linkages were not reducible at the dropping mercury electrode unless the triple bond was conjugated with an aromatic nucleus. They reported that the reduction of an acetylenic hydrocarbon generally occurred at a more negative potential than that of the corresponding ethylenic compound and therefore proceeded directly to the saturated compound.

Ono,³ however, reported two waves for phenylpropionic acid in calcium chloride media at *pH* values below 3. The ethyl ester was reported to yield two waves at *pH* values above 3. Coulometry at controlled potential showed three modes of reduction of phenylpropionic acid at *pH* 0.9: (1) a two-electron reduction at -1.1 v. vs. S.C.E. to *trans*-cinnamic acid, (2) a three-electron reduction at -1.5 v. via an intermediate free radical⁴ to diphenyl hexanedioic acid and (3) a four-electron reduction at -1.65 v. to hydrocinnamic acid.

Crain⁵ also observed two waves for a number of substituted phenylpropionates in barium acetate media. Coulometry at controlled potential confirmed that the first wave always represented reduction to the corresponding cinnamate, while the second (at least at potentials where electron transfer to the intermediate free radical proceeded much more rapidly than its dimerization) corresponded to formation of the dihydrocinnamate. In tetra-*n*-butylammonium iodide media, however, Crain obtained only a single wave, which represented a direct four-electron reduction to the hydrocinnamate.

The present investigation was designed to cast further light on the conditions required for the stepwise polarographic reduction of acetylenic bonds.

(1) Based on a thesis submitted by Seymour R. Missan to the Faculty of the Polytechnic Institute of Brooklyn in partial fulfillment of the requirements for the degree of Master of Science, June, 1959.

(2) H. A. Laitinen and S. Wawzonek, *THIS JOURNAL*, **64**, 1765 (1942).

(3) S. Ono, *Nippon Kagaku Zasshi*, **77**, 665 (1956).

(4) L. Meites, "Controlled-Potential Electrolysis," Chap. XLIX of "Physical Methods of Organic Chemistry" (Vol. I of "Technique of Organic Chemistry"), ed. by A. Weissberger, 3rd Ed., Interscience Publishers, Inc., New York, N. Y., in press.

(5) A. V. R. Crain, B.S. in Chem. Thesis, Polytechnic Institute of Brooklyn, 1957.

Experimental

Starting Materials.—*p*-Chlorophenylpropionic acid, m.p. 192-194° (reported⁶ 193-194°), was prepared by the dehydrobromination of methyl 3-(*p*-chlorophenyl)-2,3-dibromopropionate with alcoholic potassium hydroxide.

Methyl *p*-chlorophenylpropionate, m.p. 92-94°, was prepared from *p*-chlorophenylpropionic acid.⁷

Phenylpropionic acid, m.p. 135-137°, was available commercially, and methyl phenylpropionate, b.p. 128° (19 mm.), *n*_D²⁰ 1.5628, was prepared according to the general procedure.⁷

3-Phenyl-2-propyn-1-ol, b.p. 105° (2 mm.), *n*_D²⁰ 1.5882, was prepared by Meerwein-Ponndorf-Verley reduction of the corresponding aldehyde.⁸

1-Methoxy-3-phenyl-2-propyne.—Five grams (0.038 mole) of 3-phenyl-2-propyn-1-ol was added to a mixture of 6 ml. of 6 *F* sodium hydroxide and 6 ml. of pyridine. The mixture was warmed to 40° on a water-bath and 5.3 g. (0.042 mole) of methyl sulfate was added dropwise. The temperature rose to 60° and was kept there for 2 hr. while stirring. The mixture then was added to 100 ml. of water, acidified to *pH* 3 with concentrated hydrochloric acid and extracted with three successive 50-ml. portions of ethyl ether. The combined ether extracts were dried over sodium hydroxide pellets, then concentrated and distilled to give 3.5 g. (0.024 mole, 63%) of colorless 1-methoxy-3-phenyl-2-propyne, b.p. 105° (10 mm.), *n*_D²⁵ 1.5565. The product showed a strong band at 9.15 microns which was absent in the starting alcohol.

Anal. Calcd. for C₁₀H₁₀O: C, 82.16; H, 6.90. Found: C, 82.12; H, 6.98.

Commercially available diphenylacetylene, m.p. 61-62°, was used without purification.

Barium acetate, tetramethylammonium chloride and tetramethylammonium bromide were reagent grade and were used without purification. Eastman white label tetra-*n*-propyl-, -hexyl- and -heptylammonium iodide were recrystallized from ethanol. Commercial tetra-*n*-butylammonium iodide was suspended in hot ethyl acetate, filtered and dried for 4 hr. at 30° in a vacuum oven.

Tetra-*n*-amylammonium iodide was prepared by refluxing a solution of 23 g. (0.10 mole) of tri-*n*-amylamine and 22 g. (0.11 mole) of 1-iodopentane in 50 ml. of methanol for 36 hr. The mass of crystals which separated on cooling was filtered, recrystallized from ethanol and dried for 8 hr. at 35° in a vacuum oven to give 32.1 g. (0.075 mole, 75%) of white crystalline tetra-*n*-amylammonium iodide, m.p. 127.6-128.8°.

Anal. Calcd. for C₂₀H₄₄IN: C, 56.46; H, 10.42; I, 29.83; N, 3.29. Found: C, 56.50; H, 10.38; I, 29.81; N, 3.30.

Apparatus and Technique.—An accurately weighed 50-mg. sample of acetylenic compound was transferred to a 50-ml. volumetric flask, dissolved in 25% ethanol and diluted to the mark. One ml. of this solution was transferred to another similar flask, the appropriate amounts of tetra-*n*-alkylammonium salt, ethanol and barium acetate were added, and the solution then was diluted to the mark with

(6) M. S. Newman and S. N. Merrill, *THIS JOURNAL*, **77**, 5549 (1955).

(7) I. Benghiat and E. I. Becker, *J. Org. Chem.*, **23**, 885 (1958).

(8) J. J. Dudkowski and E. I. Becker, *ibid.*, **17**, 201 (1952).

water. The ethanol concentration and ionic strength were always 25% (v./v.) and 0.1 *M*, respectively, except in a few experiments with tetramethyl- and tetraethylammonium salts in which the concentration of the quaternary ion exceeded 0.1 *M* and in which no barium acetate was added. A portion of the solution was transferred to an H-cell of the type described by Lingane and Laitinen⁹; this was provided with a saturated calomel reference electrode and a saturated potassium chloride-4% agar bridge and was immersed in a water thermostat at $23 \pm 0.05^\circ$. Deaeration was accomplished by bubbling nitrogen through the solution for 10 minutes.

Polarograms were obtained with a Model G1 Electro-Polarizer (Instrument Division, American Optical Company). In 25% ethanol containing 33.3 m*F* barium acetate, the capillary characteristics at $E_{d.s.} = \pm 0$ v. vs. S.C.E. were $m = 2.01$ mg./sec. and $t = 3.43$ sec. Replacing the barium acetate by 0.1 *F* tetra-*n*-butylammonium iodide caused no significant change in the value of *m*. Half-wave potentials and diffusion currents were measured from the recorded polarograms by conventional methods.

Data¹⁰ and Discussion

Two waves of essentially equal height were obtained on polarograms of methyl *p*-chlorophenylpropionate in 25% ethanol containing 0.1 *F* potassium chloride, potassium iodide, tetramethylammonium chloride (Fig. 1, curve 1) or tetraethylammonium bromide (Fig. 1, curve 2), or 0.033 *F*

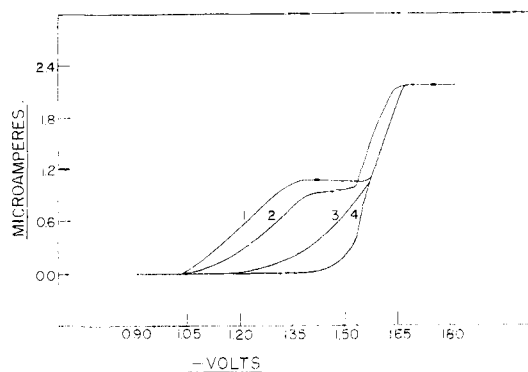


Fig. 1.—Polarograms of methyl *p*-chlorophenylpropionate in 0.1 *F* (a) tetramethylammonium chloride, (b) tetraethylammonium bromide, (c) tetra-*n*-propylammonium iodide and (d) tetra-*n*-butylammonium iodide.

barium acetate or barium iodide. However, only one wave was obtained in 0.1 *F* tetra-*n*-butylammonium iodide (Fig. 1, curve 4) or nitrate; its height was almost exactly equal to the total height of the double wave secured in the other media. Plots of wave height *versus* the square root of the height of the column of mercury above the capillary tip showed that the height of each wave in 0.033 *F* barium acetate and of the single wave in 0.1 *F* tetra-*n*-butylammonium iodide was diffusion-controlled rather than adsorption- or kinetic-controlled.

Although a polarogram of methyl *p*-chlorophenylpropionate in 0.1 *F* tetramethylammonium chloride (Fig. 1, curve 1) is almost perfectly superimposable

(9) J. J. Lingane and H. A. Laitinen, *Ind. Eng. Chem., Anal. Ed.*, **11**, 504 (1939).

(10) Table I, listing the half-wave potentials and diffusion currents obtained, has been deposited as Document number 6303 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting in advance \$1.25 for photo-prints or \$1.25 for 35-mm. microfilm by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

on the curves obtained with solutions containing only barium or potassium salts, the same concentration of any other of the tetraalkylammonium ions causes the shape of the polarogram to change considerably. As the size of the tetraalkylammonium ion increases, the diffusion current of the first wave decreases and its half-wave potential shifts to more negative values, until eventually the two waves merge into a single one which, as in the work of Laitinen and Wawzonek,² represents a direct four-electron reduction to the saturated compound. In view of Crain's demonstration⁵ that the half-wave potential of the corresponding first wave of methyl phenylpropionate is entirely independent of *pH* over the range involved here, it is clear that this variation cannot be attributed to the relatively small buffer capacities of the supporting electrolytes employed.

Further insight into the nature of this phenomenon was gained from experiments in which the concentration of tetraalkylammonium ion was varied. Figure 2 shows the results obtained with five of the quaternary ions. The variations of the

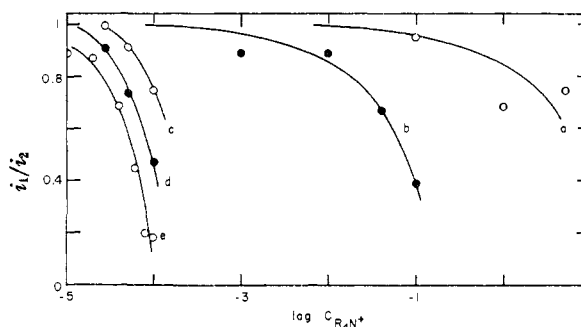


Fig. 2.—Effects of (a) tetramethylammonium, (b) tetra-*n*-propylammonium, (c) tetra-*n*-butylammonium, (d) tetra-*n*-amylammonium and (e) tetra-*n*-hexylammonium ions on the ratio of the heights of the waves of methyl *p*-chlorophenylpropionate.

ratio of the wave heights always involved a growth of the second wave at the expense of the first; except in the most concentrated solutions of tetramethyl- and tetraethylammonium salts, whose higher viscosities caused the heights of both waves to decrease somewhat, the over-all wave height always remained very nearly constant. Even 5 *F* tetramethylammonium chloride caused only a relatively minor change in the shape of the polarogram. But the same change was produced by only about 0.03 m*F* tetra-*n*-hexylammonium iodide, which shows the striking effect of the size of the quaternary ion.

Along with this decrease in the height of the first wave and concomitant growth of the second wave, there is a fairly rapid shift of the half-wave potential of the first wave toward more negative values. As the half-wave potential of the second wave meanwhile shifts toward slightly more positive values, the two waves coalesce as the concentration of tetraalkylammonium ion is increased. This makes it somewhat difficult to find the concentration of quaternary ion that just causes the first wave to disappear, but approximate values for the different ions studied are $(\text{CH}_3)_4\text{N}^+$, > 5 *M*; $(\text{C}_2\text{H}_5)_4\text{N}^+$, 1

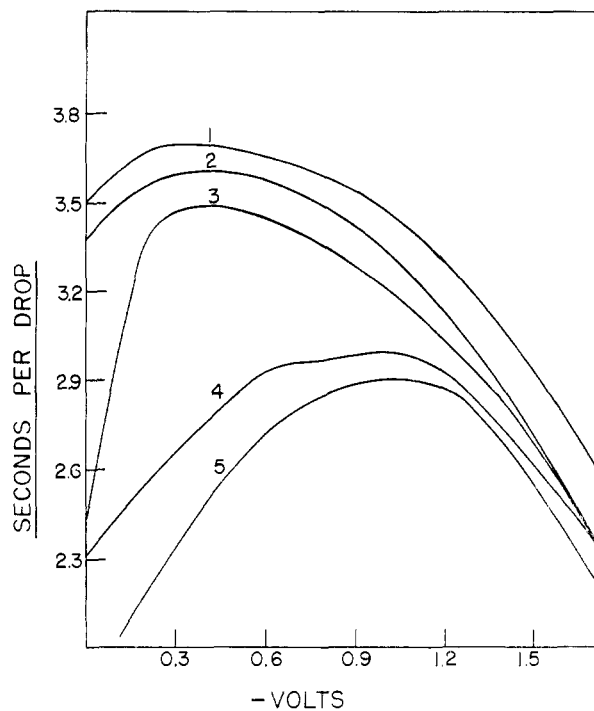


Fig. 3.—Electrocapillary curves of solutions containing (a) 33.3 mF barium acetate, (b) 0.1 F tetramethylammonium chloride, (c) 0.1 F tetraethylammonium bromide, (d) 0.1 F tetra-*n*-propylammonium iodide and (e) 0.1 F tetra-*n*-butylammonium iodide.

M ; $(C_3H_7)_4N^+$, 0.2 M ; $(C_4H_9)_4N^+$, 0.01 M ; $(C_5H_{11})_4N^+$, 0.0004 M ; $(C_6H_{13})_4N^+$, 0.0002 M ; $(C_7H_{15})_4N^+$, 0.0002 M . It is interesting to note that the tetra-*n*-hexyl- and -heptylammonium ions, which are nearly equally effective in suppressing the first wave, are also shown by models to be of very nearly equal size.

One important corollary of these results to the organic polarographer is that, until further investigations have circumscribed the generality of phenomena of this type, extreme caution should be exercised in deducing conclusions regarding reduction mechanisms from data obtained in the presence of long-chain tetraalkylammonium ions. Tetra-*n*-butylammonium salts are certainly very useful in practical polarographic analyses because of the very negative potentials which they render attainable. However, their utility in electro-chemical and -kinetic investigations may be far more limited than has been realized.

The changes in half-wave potentials and relative wave heights were very closely related. For each of the seven quaternary ions studied, the half-wave potentials of the two waves were measured in a solution in which i_1/i_2 was 0.70 ± 0.05 and were found to be -1.30 ± 0.04 and -1.59 ± 0.01 v., respectively; no significant effect of the length of the alkyl chain could be detected. These values may be compared with those obtained in 0.033 F barium acetate, which were -1.194 and -1.613 v.

Plots of $E_{d.e.}$ vs. $\log i/(i_d - i)$ for the two waves obtained in 0.033 F barium acetate were strictly linear and had slopes of -116 mv. for the first wave and -53 mv. for the second wave. A similar plot

for the single wave in 0.1 F tetra-*n*-butylammonium iodide was also linear; its slope was -64 mv. Thus, αn_a was 0.51 for the first and 0.90 for the second wave in barium acetate; for the single wave in tetra-*n*-butylammonium iodide it was 1.09. If, in the absence of any grounds for a contrary belief, it is assumed that α , the transfer coefficient, has the customary value of approximately 0.5 in each case, it follows that n_a , the number of electrons involved in the rate-determining step, is 1 for the first wave in barium acetate and 2 for each of the other waves. It thus appears that the effect of the tetra-alkylammonium ions may be described phenomenologically in terms of barring a one-electron initial step in favor of one involving two electrons.

That various tetraalkylammonium ions are capillary-active and are therefore adsorbed onto the surfaces of mercury electrodes has been reported by several authors.¹¹⁻¹³ In the present work it was found that 0.1 F tetramethylammonium chloride gave an electrocapillary curve nearly, though not exactly, coincident with that of 0.033 F barium acetate. Solutions containing 0.1 M tetraethyl-, -*n*-propyl- or -*n*-butylammonium ion displaced the negative branch of the electrocapillary curve still further in the direction of increasing capillary activity, as is shown in Fig. 3. The longer chain quaternary ions exerted even more pronounced effects. For example, the negative branch of the electrocapillary curve was displaced to a greater extent by 0.0002 M tetra-*n*-hexylammonium ion than by 0.1 M tetra-*n*-butylammonium ion. Because the concentration of iodide ion, which is also strongly capillary-active, though at more positive potentials, was varied along with that of the quaternary ion in these experiments, the electrocapillary curves obtained with the different tetraalkylammonium ions were not exactly geometrically similar. As closely as could be told, however, the concentration of a tetraalkylammonium ion required to produce a given shift of the negative branch of the electrocapillary curve appeared to be of at least the same order of magnitude as that which caused a given change in the relative heights of the two propionate waves or in the half-wave potential of the first wave.

The direction of the shift of half-wave potential with increasing adsorbability of the quaternary ion is precisely the opposite of that predicted by the theory of Reinmuth, Rogers and Hummelstedt.¹⁴ Nor could any evidence be found for the systematic variation of αn_a with potential predicted by that theory at concentrations of tetraalkylammonium ion too low to cause actual coalescence of the two waves. In fact, though the observations that can be made are limited in precision, it appears that αn_a for the first wave under these conditions decreases slightly instead of increasing as the theory predicts.

In this theory it is assumed that the mechanism

(11) (a) G. Sutra, *J. chim. phys.*, **43**, 189 (1946); (b) L. Meites and T. Meites, *THIS JOURNAL*, **73**, 177 (1951).

(12) M. A. Loshkarev and A. A. Kryukova, *Zhur. Fiz. Khim.*, **31**, 452 (1957).

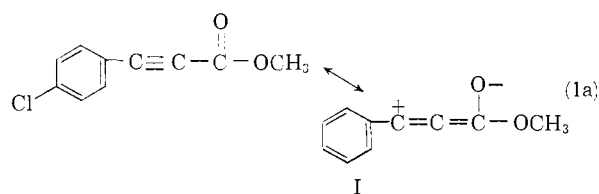
(13) L. E. I. Hummelstedt and L. B. Rogers, *J. Electrochem. Soc.*, **106**, 248 (1959).

(14) W. H. Reinmuth, L. B. Rogers and L. E. I. Hummelstedt, *THIS JOURNAL*, **81**, 2947 (1959).

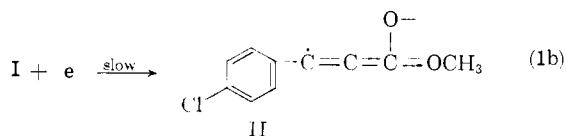
of the electrode reaction is unchanged by the addition of adsorbable material, and the changes in half-wave potential and wave shape occurring when this is true are attributed to the effects of the adsorbed material on the capacity of the electrical double layer. The disparities between theoretical prediction and experimental observation with respect to the first wave of methyl *p*-chlorophenylpropiolate indicate that the fundamental assumption is not obeyed, and that the addition of quaternary ions actually modifies the reaction mechanism. On the other hand, the second wave appears to obey the predictions of this theory. It therefore appears that the mechanism of the reduction of cinnamate to dihydrocinnamate is unaltered by the presence of adsorbed quaternary ions. These conclusions are embodied in the interpretation suggested below.

As neither diphenylacetylene nor 1-methoxy-3-phenyl-2-propyne was found to be reducible at the dropping electrode from 0.033 *F* barium acetate solutions, it is evident that the presence of the electronegative ester group conjugated with the triple bond plays an important role in the reducibility of methyl *p*-chlorophenylpropiolate. Indeed, molecular models indicate that the 1,2-addition of electrons to the triple bond in this molecule would be difficult, because steric hindrance would constitute a considerable bar to the necessary orientation of the rigid planar triple bond on the electrode surface. This indicates that the addition of a pair of electrons to this compound probably proceeds by a 1,4-mechanism involving one of the oxygen atoms of the ester group. On the other hand, molecular models indicate that the double bond in either *cis* or *trans* methyl cinnamate is much less hindered, so that the reduction of either of these molecules may well involve simple 1,2-addition across the double bond.

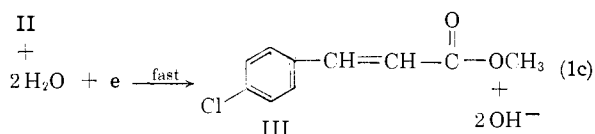
In view of these considerations, the following mechanism of reduction of methyl *p*-chlorophenylpropiolate is proposed as being in accord with all of the experimental data. It is suggested that the first wave in barium acetate media, which was shown above to involve a one-electron rate-determining step, proceeds by the mechanism



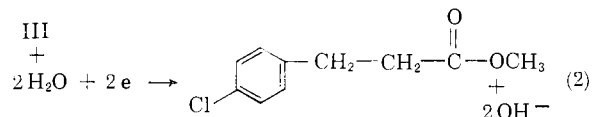
The negatively charged oxygen atom would be repelled from the electrode surface, and attack would therefore probably occur at the electrophilic carbon atom



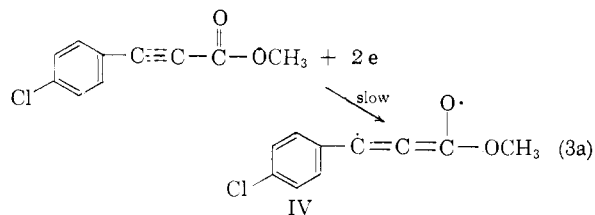
followed by a sequence of comparatively fast reactions which could be represented by



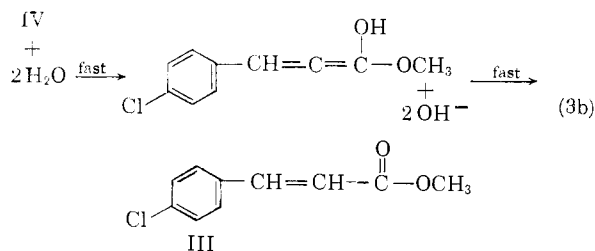
The second wave in barium acetate media involves a two-electron rate-controlling step. This may, as was stated above, consist of a direct 1,2-addition of electrons across the double bond, or it may equally well consist of 1,4-addition across the conjugated C=C-C=O system. In either case, of course, the over-all stoichiometry of this step is represented by the equation



In the presence of a layer of adsorbed tetraalkylammonium ions, however, the orientation of I necessary for the occurrence of step (1b) would be much more difficult, partly for purely mechanical reasons and partly because of repulsion of the electrophilic center by the cations adsorbed on the electrode surface. Under these conditions the rate of step (1b) would be greatly decreased, and it is suggested that this rate-determining step is replaced by this two-electron step involving 1,4-addition across the conjugated system



followed by rapid uptake of protons and rearrangement



Thus a molecule of methyl *p*-chlorocinnamate is formed at the electrode surface, and this then undergoes further reduction to the dihydrocinnamate according to (2). That this further reduction is immediate seems to suggest that the reduction of the cinnamate also proceeds by a 1,4-mechanism; otherwise, if the above proposals are correct, it would hardly be expected that the necessary reorientation of the molecule with respect to the electrode surface could occur as rapidly as appears to be the case.