Use of Tetrabutylammonium Tribromide for Voltametric Titration of Unsaturation in Vegetable Oils and Fatty Acids

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The use of tetrabutylammonium tribromide as reagent for bromination of carbon-carbon double bonds of fatty acids and vegetable oils, followed by a voltametric titration of tribromide and bromide ions, has been studied. This method is easy and fast, and results show good accuracy and high sensitivity.

KEY WORDS: **Bromination, carbon-carbon double bonds, fatty acids, tetrabutylammonium tribromide, vegetable oils, voltametric titration.**

For some years, tetrabutylammonium tribromide (henceforth called $TBABr_3$) has been used as a brominating agent in synthetic organic chemistry. Compounds such as ketones (1), phenols (2), aromatic amines (2) and alkenes (1) have been brominated with this reagent. The ease of handling $TBABr_3$, which is an anhydrous and stable solid, and the high rate of reaction at room temperature in various solvents have suggested the advantages of using this reagent in quantitative analytical work, especially for alkenes.

$$RCH = CHR' + TBABr_3 \rightarrow RCHBr - CHBrR' + TBABr \quad [1]$$

Because bromide and tribromide ions are involved, an electrochemical method seems to be the most appropriate method to determine the amount of added bromine.

In a previous paper (4), we reported the simple and easy voltametric monitoring of Br^- and Br_3^- concentrations during the bromination of alkenes by Br_3^-. The present investigation shows the use of $TBABr_3$ for the direct electrochemical titration of carbon-carbon double bonds of fatty acids and vegetable oils.

Most titration procedures for the determination of carbon-carbon double bonds involve addition of hydrogen or halogen to the double bond. Several investigators (5,6) have described coulometric procedures for bromination of olefins. Results were not quantitative, and agreement with standard methods was not always good. The literature gives few convenient procedures for direct coulometric bromination of unsaturated fatty acids and food oils (7,8). Recently, the use of propylene carbonate as a solvent for coulometric bromination of fatty acids and oils has been studied. Titration results are good but propylene carbonate is relatively difficult to purify, and the impurities may consume bromine. Moreover, most vegetable oils are not sufficiently soluble in neat propylene carbonate (9).

EXPERIMENTAL PROCEDURES

The cell, the rotating platinum microelectrode and the potentiostat used for the titrations were as described previously (10). $TBABr_3$, CH_3CN (99+% spectrophotometric grade), alkenes, oleic and linoleic acids were obtained from Janssen Chimica (Noisy le Grand, France), and vegetable oils were purchased locally in food stores. Bu_4NClO_4 (puriss; electrochemical grade) was purchased from Fluka A.G. (Buchs, Switzerland). We used a 0.1 M solution of this electrolyte. $TBABr_3$ was dissolved in dry chloroform and purified by washing, first with an aqueous $NaHCO_3$ (10%) solution, then with water until pH 7. The chloroform solution was then dried over Na_2SO_4 and finally evaporated. Pure $TBABr_3$ displayed a melting point of 84°C.

As described in a previous work (10), Figure 1 represents the voltametric behavior of bromide ions (b) and tribromide ions (c). Bromide ions are oxidized in two successive steps corresponding to two waves (located, respectively, at +0.41 V and +0.75 V *vs.* Ag/Ag^+). the voltamogram of $TBABr_3$ displays a reduction wave at −0.1 V and an oxidation wave at +0.67 V (*vs.* Ag/Ag^+). All of the processes correspond to slow electron transfers. These results are in agreement with the results of Popov and Geske (11), who proposed the following electrochemical reactions:

$$6\ Br^- - 4e^- \underset{I}{\overset{I'}{\rightleftharpoons}} 2\ Br_3^- \quad [2]$$

$$2\ Br_3^- - 2e^- \underset{II,\ II'}{\rightleftharpoons} 3\ Br_2 \quad [3]$$

The intensities of the $i_{DI'}$, $i_{DII'}$, $i_{DI'}$ and $i_{DII'}$ diffusion currents are proportional to the concentrations of Br^- and Br_3^-.

Calibration curves are characterized by slopes and correlation coefficients, which are collected in Table 1. Calibration curves were obtained from eight standard solutions with concentrations between 10^{-4}M and 2.10^{-3}M. Six independent measurements were performed for each concentration, and the slope correlation coefficients were determined from the results.

The results show that voltametry allows the simultaneous determination of Br^- and Br_3^- concentrations in

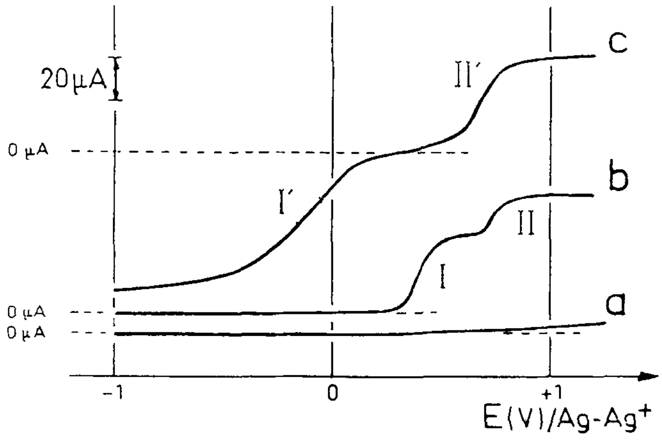

FIG. 1. Voltametric curves obtained in $CH_3CN + Bu_4\ NClO_4$ 0.1 M with a platinum microelectrode at 500 rpm (sweeping speed: 20 mV/s). a, Supporting electrolyte curve; b, 2.3 10^{-3}M TBABr; c, 1.5 10^{-3}M $TBABr_3$.

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TABLE 1

Calibration Curves and Correlation Coefficients

Reactive species	Wave	E (V) Ag/Ag$^+$	Slope (ν A/m mol)	Correlation coefficient
Br_3^-	Red (I)	−0.1	40.0 ± 2.1	0.995
	Ox (II)	+0.71	24.6 ± 0.9	0.999
Br^-	Ox (I)	+0.39	17.7 ± 0.5	0.999
	Ox (II)	+0.75	9.0 ± 0.1	0.999

TABLE 2

Bromination of Alkenes and Titration by Voltametry

Compound	Product (percent recovery)	Time (min)
Styrene	99	10
1-Hexene	99	3
1-Octene	100	3
Cinnamic acid	96	15
Oleic acid	100	12
Linoleic acid	101[a]	13

[a] Calculated on basis of two moles of TBABr$_3$ consumed per mole of linoleic acid. This acid has two double bonds that are completely brominated.

the solution. It is thus possible to monitor an alkene bromination reaction by TBABr$_3$ with this technique. In the course of such a reaction, the I′ reduction wave (reduction of Br_3^- into Br^-) will decrease due to the consumption of Br_3^-. Conversely, the formation of Br^- ions will result in the appearance of an increasing oxidation wave (wave I, oxidation of Br^- in Br_3^-). There are thus two simultaneous ways to determine the bromination of a carbon-carbon double bond: (i) the titration of remaining tribromide ions; and (ii) the titration of formed bromide ions.

RESULTS AND DISCUSSION

In our previous paper we showed that styrene was efficiently monitored by this electrochemical method (10). The percentage of double bond titrated was 99%. The same method has been used with other alkenes after we verified that these compounds give no oxidation or reduction wave between −1V and +1V. Voltametric monitoring of Br^- and Br_3^- concentrations during the bromination was carried out as described before. To verify the validity of our method before applying it to oils, we brominated various alkenes (some of them with phenyl or carboxyl substituents) at room temperature. We observed that the expected dibrominated compounds are quantitatively obtained. A similar result is obtained with two unsaturated acids (oleic and linoleic acids). All the results of bromination and of direct titration of these unsaturated compounds are reported in Table 2. The reactions were quantitative.

Determination of carbon-carbon double bonds of vegetable oils. We also have verified that these oils give no oxidation or reduction waves between −1V and +1V. TBABr$_3$ (1 g) was dissolved into 5 mL of dry deaeratd CHCl$_3$ (oxygen gives reduction waves that hinder the titration). The solution was stirred and 400 mg of oil were added. The chloroform solution volume was adjusted to 10 mL with deaerated CHCl$_3$ (the concentration of TBABr$_3$ was thus equal to 0.2 M) and stirred for about 15 min.

The reaction was followed by titration of 100-μL samples from the reaction medium. These samples were immediately introduced under Argon into the electrolysis cell, which contained 10 mL of CH$_3$CN (with 0.1 M Bu$_4$CNlO$_4$ supporting electrolyte). In all cases the solutions were protected from direct exposure to light to avoid possible polymerization. Titrations carried out every 2 min showed that all the bromination of oils is completed in about 15 min (for example, the voltametric titration of a sample of sunflower oil is reported in Fig. 2). Results shown in terms of bromine number (g Br$_2$/100 g sample) are listed in Table 3. The comparison of titrations per-

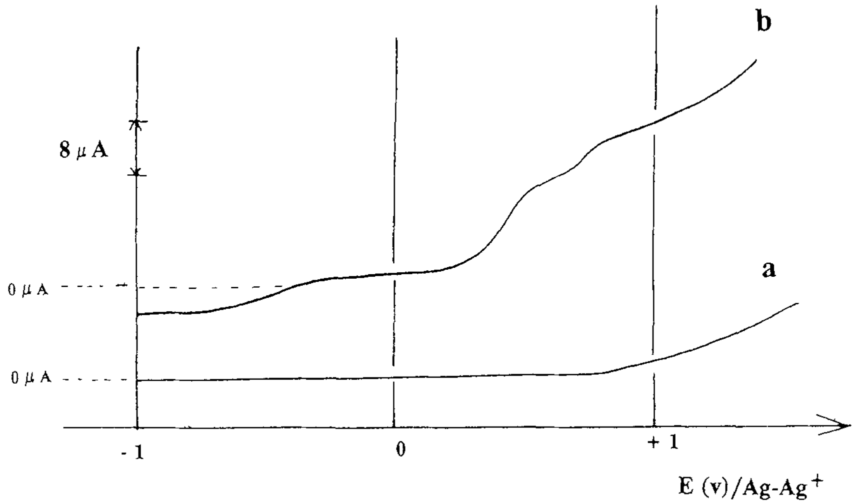

FIG. 2. Bromination of sunflower oil in CH$_3$CN + Bu$_4$ NClO$_4$ 0.1 M with a platinum microelectrode at 500 rpm (sweeping speed: 20 mV/s). a, Supporting electrolyte + sunflower oil; b, supporting electrolyte + sunflower oil + TBABr$_3$.

TABLE 3

Titration of Carbon-Carbon Double Bonds of Various Oils and Fatty Acids

Sample[a]	Nominal[b]	Wijs[c]	Voltametry[d]	
			α Br_3^-	β Br^-
Oleic acid	56.7	54.5 ± 0.2	56.2 ± 0.5	55.5 ± 0.5
Linoleic acid	115.3	99.3 ± 0.3	120.5 ± 0.7	120.0 ± 0.6
Olive oil	49.8–57.4	56.6 ± 0.3	58.4 ± 0.4	58.0 ± 0.5
Sunflower oil	76.9–88.8	93.4 ± 0.5	88.0 ± 0.5	92.0 ± 0.5
Corn oil	69.9–80.6	85.0 ± 0.6	82.3 ± 0.3	84.0 ± 0.4
Peanut oil	55.4-61.7	61.9 ± 0.3	61.4 ± 0.3	60.1 ± 0.5
Nut oil	—	103.0 ± 0.5	105.0 ± 0.3	105.3 ± 0.4

[a] Commercial oils used as received.

[b] The nominal value shown for oleic and linoleic acids was calculated from their molecular formulas, and the values for the other samples (oils) were taken the International Critical Tables (ref. 12).

[c] Results by this procedure (ref. 13) are the average for three replicate analyses.

[d] Data are the average for six replicate titrations.

formed with and without prior borohydride reduction (under these conditions there is no reduction of $TBABr_3$) allowed us to verify that no carbonyls were present in the samples. To confirm this we performed the following experiments: (i) a known amount of oil (olive oil) was brominated by $TBABr_3$; (ii) a known quantity of acetophenone was added prior to bromination to the same amount of oil (the amount of titrated $TBABr_3$ corresponds to the bromination of oil and acetophenone); and (iii) the same experiment as in (ii) was repeated with a prior borohydride reduction (the titration result was identical to the value obtained without carbonyl addition).

The voltametry results of oils shown in Table 3 are in good agreement with both the nominal values and the Wijs results. The values obtained from the bromide and tribromide waves also are in good agreement for each sample analyzed. All the samples appeared to react quickly and quantitatively with $TBABr_3$. The brominated sample underwent no apparent further reaction. The good agreement between the values obtained from the two titrations of remaining tribromide ions and of formed bromide ions proves that competitive substitution reactions do not take place. Effectively, the following substitution reaction would give two bromide ions for each tribromide ion consumed:

$$R - H + Br_3^- \rightarrow R - Br + 2\,Br^- + H^+ \qquad [4]$$

Thus, a near-quantitative bromination of carbon-carbon double bonds of oils is obtained easily at room temperature in dry chloroform when $TBABr_3$ is used as bromination reagent. This reaction, followed by a fast voltametric titration, constitutes a good analytical method of determination of carbon-carbon double bonds in vegetable oils.

REFERENCES

1. Fournier, M., F. Fournier and J. Berethelot, *Bull. Soc. Chim. Belg.* *93*:157 (1984).
2. Berthelot, J., C. Guette, P-L. Desbéne, J-J. Basselier, P. Chaquin and D. Masure, *Can. J. Chem.* *67*:2061 (1989).
3. Berthelot, J., C. Guetle, P.L. Desbéne, J. J. Basselier, P. Chaquin and D. Masure, *Ibid.* *64*:464 (1990).
4. Berthelot, J., J-J. Basselier, P-L. Desbène and A. Desbène-Monvernay, *Analysis* *15*:22 (1987).
5. Leisey, F.A., and J.F. Grutsch, *Anal. Chem.* *28*:1553 (1956).
6. Miller, J.W., and D.D. DeFord, *Ibid.* *29*: (1957).
7. Baumann, F., and D.D. Gilbert, *Ibid.* *35*:1133 (1963).
8. Kratochvil, B.P., K. Chattopadhyay and R.D. Krause, *Ibid.* *48*:568 (1976).
9. Cheney, M.C., and K.S. Kletcher, *Ibid.* *51*:807 (1979).
10. Desbène-Monvernay, A., J. Berthelot and P-L. Desbène, *J. Chem. Educ.* *64*:86 (1987).
11. Popov, A.I., and D.H. Geske, *J. Am. Chem. Soc.* *80*:5346 (1958).
12. *International Critical Tables, Vol. II*, McGraw Hill, New York, 1927, p. 201.
13. Polgar, A., and J.L. Jungnickel, *Organic Analysis, Vol. 3*, edited by J. Mitchell, I.M. Kolthoff, E.S. Proskauer and A. Weissberger, Interscience, New York, 1956, p. 222.

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