Kinetics of chemical degradation of isoxaflutole: influence of the nature of aqueous buffers (alkanoic acid/sodium salt *vs* phosphate)†

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Abstract: A kinetic study of the chemical degradation of isoxaflutole (5-cyclopropyl-1,2-oxazol-4-yl ααα-trifluoro-2-mesyl-*p*-tolyl ketone) into its diketonitrile derivative (DKN), which is its active herbicide principle, in organic buffers at different pH values was carried out using a HPLC/UV detection method. The values of the pseudo-first-order rate constants K_{obs} for the reaction were calculated and compared with those previously obtained in inorganic buffers. In both cases, K_{obs} was found to be dependent on pH and temperature, but at pH 5.2 the degradation of isoxaflutole in CH_3COOH/CH_3COONa buffers was considerably faster than in KH_2PO_4/Na_2HPO_4 buffers, indicating that the compound was sensitive to the nature of the reagents used to prepare buffered solutions. The influence of phosphate and acetate concentrations and the influence of the R-substituent in RCOOH/RCOONa buffers were investigated. For the HA/A^- buffers studied, the values of K_{obs} were linearly dependent on HA and A^- concentrations, which meant that the degradation of isoxaflutole was subject to general catalysis. The values of K_{obs} were also found to be dependent on the number and the position of the CH_3 groups of the R-substituent. The known degradation product of DKN (a benzoic acid derivative) was not detected throughout this study.

Keywords: isoxaflutole; diketonitrile derivative; chemical degradation; basic catalysis; general catalysis

1 INTRODUCTION

Isoxaflutole (5-cyclopropyl-1,2-oxazol-4-yl ααα-trifluoro-2-mesyl-*p*-tolyl ketone; Fig 1) is a new herbicide recently developed by Aventis and used in corn and sugarcane. It provides effective control of both grass and broad-leaf weeds after pre-emergence application at a relatively low rate (c 75 g ha^{-1}).

Preliminary studies (Reference 1 and Rhône–Poulenc Agro, pers comm) have shown that degradation of isoxaflutole in various matrices (water, soil, vegetation) leads to a diketonitrile derivative (3-cyclopropyl-1-(ααα-trifluoro-2-mesyl-*p*-tolyl)-1,3-dioxopropane-2-nitrile; DKN, Fig 1) by an opening of the isoxazole ring. This diketonitrile derivative is the active herbicidal principle and acts by inhibiting a specific enzyme of carotenoid synthesis (4-hydroxyphenylpyruvate dioxygenase, HPPD). This inhibition leads to bleaching in susceptible weed species, followed by

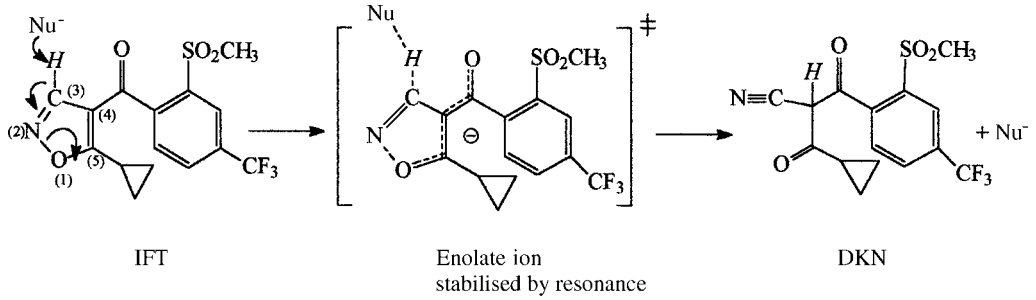

Figure 1. Concerted one-stage E2-type mechanism of the degradation of isoxaflutole (IFT) into the diketonitrile (DKN).

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growth suppression and necrosis. In plants, the diketonitrile is rapidly converted into the inactive acid derivative ααα-trifluoro-2-mesyl-*p*-toluic acid (BA); such a metabolic pathway seems to occur also in soil. (Rhône–Poulenc Agro, pers comm)

Previous work[2] has shown that the degradation of isoxaflutole in aqueous solutions followed pseudo-first-order kinetics, was catalysed by hydroxide ions and activated by temperature; log K_{obs} was linearly dependent on pH, but the discontinuities observed showed that the nature of the buffer constituents had an effect on the rate of the degradation. In a critique of the OECD and EPA methods recommended for the determination of the rates of hydrolysis of chemicals in the environment, Grayson[3] pointed out the importance of experimental conditions such as temperature, pH, buffer type and concentration, since these can lead to variations in the values observed for rate constants.

The objective of the present study was to extend understanding of isoxaflutole behaviour in aqueous media by determining the way in which organic acids and/or their conjugate bases catalyse its degradation in water; various ionic strengths and concentrations of the buffer constituents (phosphate and acetate) and several R-substituents (for buffers RCOOH/RCOONa) were studied. Experiments were carried out at 30 °C and at a number of pH values between 4 and 7.

2 MATERIALS AND METHODS

2.1 Chemicals

Isoxaflutole, DKN and BA of analytical standard purity were provided by Aventis CropScience (Ongar, UK). The solvents (methyl alcohol and acetonitrile for HPLC) were supplied by Carlo Erba. Buffered aqueous solutions were prepared with reagents of purity ≥99% (potassium chloride and potassium dihydrogen phosphate were supplied by Prolabo, succinic acid by Fluka, isobutyric acid, trimethylacetic acid, propionic acid and *n*-butyric acid by Aldrich, sodium hydroxide by Carlo Erba, acetic acid and disodium hydrogen phosphate anhydrous by Merck) and with sterile and pyrogen-free water (B Braun Medical SA). Because of the low solubility of isoxaflutole in water (about 6 mg litre^{-1} at 20 °C), solutions containing 10 mg litre^{-1} ($2.78\ 10^{-5}$ M) of this compound were prepared from methanolic solutions (1000 mg litre^{-1}), giving a methanol content of 10 ml litre^{-1} in the final aqueous solutions.

2.2 Degradation in aqueous solutions

In order to evaluate the influence of the nature of buffer constituents on the hydrolysis of isoxaflutole, the above solutions were kept in the dark at a constant temperature of 30 °C under sterile conditions, and no pH variation was observed during any of the experiments. Samples were removed at appropriate times and analysed by HPLC/UV without further processing.

2.3 Analytical procedure

Samples were analysed by HPLC/UV, using a Shimadzu LC-10A pump with SPD 10AVP autoinjector (injected volume: 20 μl), the compounds were detected by their UV absorbance at 267 nm (isoxaflutole and BA) and 290 nm (DKN) using a Shimadzu SPD-10AVP UV detector. The column used was 5-μm C_{18} Hypersil ODS stationary phase 250 mm × 4.6 mm, from Supelco, the mobile phase was acetonitrile + water + trifluoroacetic acid (48 + 52 + 0.5 by volume) delivered at 1 ml min^{-1}. Under these conditions, the retention times of isoxaflutole, DKN and BA were 14.6, 13.7 and 4.9 min, respectively. Identification and analysis were performed by injection of analytical standards for comparison. Data were collected using Star software (Varian).

2.4 Quality criteria of the method

At 267 nm, the limit of detection (LOD) was 0.05 and 0.12 mg litre^{-1} for isoxaflutole and BA, respectively, and that for DKN at 290 nm was 0.07 mg litre^{-1}. The limit of quantification (LOQ) was defined as the sample concentration required to give a signal-to-noise ratio of 6:1 and corresponded to twice the LOD for each compound. Linearity of the detector response was evaluated at the two wavelengths used in this study by injecting solutions containing the three analytical standards at five different concentrations for each compound varying from 1–100 times the LOQ. Each injection was duplicated and the entire procedure repeated the following day. The response of the detector was found to be linear, with coefficients of determination (r^2) greater than 0.9993 for the three compounds. We verified that no compound interfered with isoxaflutole and its derivatives during chromatographic analysis by injecting blank (analyte-free) buffered solutions.

3 RESULTS AND DISCUSSION

3.1 Influence of ionic strength

There are significant electrostatic interaction forces between the ions in buffered solution. The ionic strength μ is given by the expression

$$\mu = 1/2\Sigma(c_i \cdot z_i^2)$$

where c_i is the concentration of each ion (M), and z_i, is its charge. The influence of ionic strength on K_{obs} has been studied for phenylbutazone and cefotaxime[4] and found to be negligible at pH 2.2 and pH 6.0, but significant at higher pH values. In the present work, the effect of μ was studied in five phosphate buffers ($[KH_2PO_4] = [Na_2HPO_4] = 0.05$ M) at pH 6.7, with an initial isoxaflutole concentration of 10 mg litre^{-1} and at the same temperature (30 °C), μ being varied from 0.2 to 0.4 M by adding increasing quantities of

potassium chloride. No difference in K_{obs} values was observed and, in these conditions, the average half-life of isoxaflutole was 34 (±3) h.

3.2 Differences in the rate of the degradation with respect to the buffers' reagents

In a previous study,[2] the degradation of isoxaflutole was studied in aqueous solutions prepared with inorganic buffers over a wide range of pH values (1.8–10.1) and at three temperatures (22, 30 and 50 °C), and shown to follow pseudo-first-order kinetics:[5]

$$C = C_0 \exp(-K_{obs} \cdot t) \quad (1)$$

where C is the concentration of isoxaflutole (M) at time t, C_0 its initial concentration (M), K_{obs} the observed rate constant of the reaction (h^{-1}) and t the incubation time (h). The effect of temperature on the rate of the degradation of isoxaflutole in aqueous solutions was determined by using Arrhenius' law:

$$K_{obs} = A \exp[-E_a/(RT)] \quad (2)$$

where A is a specific constant of the reaction (h^{-1}), E_a the activation energy in (J mol^{-1}), R the universal gas constant (8.314J mol^{-1} K^{-1}), and T the absolute temperature (K). The values of E_a were calculated from the slope of ln K_{obs} against ($1/T$) and the corresponding activation entropies $\Delta S^{\neq}$ were calculated from the y-intercept of the plot of ln (K_{obs}/T) against ($1/T$).[5] Thus, it was found that the degradation of isoxaflutole in aqueous solutions with inorganic buffers was catalysed by the concentration of hydroxide ions and activated by temperature. Opening of the isoxazole ring led to the diketonitrile derivative DKN, and the acid derivative, BA, was not detected during any of the experiments. The influence of pH on the observed rate constant was more difficult to determine because of discontinuities in the plots of log K_{obs} *vs* pH. Thus, for each of the three temperatures, the slope of log K_{obs} against pH varied with respect to the buffers used (KH_2PO_4/Na_2HPO_4 for $5.2 \leq pH \leq 8.0$ and H_3BO_3/NaOH for $8.3 \leq pH \leq 10.1$). Such discontinuities have been observed in the hydrolysis of sulfonylureas and attributed to the different reactivities of dissociated and undissociated forms of these herbicides with respect to water molecules.[6] These discontinuities also corresponded to changes in the buffer reagents used, indicating that the nature of these reagents could have an important effect on the reactivity of the sulfonylureas, as also seemed to be the case for isoxaflutole in the present study.

To extend understanding of the mechanism of isoxaflutole degradation in water, additional studies were conducted in aqueous buffered solutions prepared with organic acids and their conjugate bases. As buffers prepared with CH_3COOH/CH_3COONa are widely used in kinetic experiments, the degradation of isoxaflutole in such solutions was studied at two pH values and at 22, 30 and 50 °C. As expected, the degradation of isoxaflutole followed pseudo-first-order kinetics, but the values of the rate constant K_{obs} were much higher than those obtained with a KH_2PO_4/Na_2HPO_4 buffer for the same pH 5.2 (Table 1).

The similar values of E_a indicated that the mechanism of the reaction was a concerted one-stage E2 type (Fig 1) in both the organic and inorganic buffers, corresponding to the usual reaction undergone by isoxazoles unsubstituted in the 3-position.[7,8] The difference observed in $\Delta S^{\neq}$ values showed that, in the presence of RCOOH and $RCOO^-$, the enolate ion formed during the reaction was as constrained as isoxaflutole at such pH values ($\Delta S^{\neq}$ close to zero), whereas in phosphate buffer the enolate ion was apparently more constrained (highly negative value of $\Delta S^{\neq}$).

Under the above conditions, the increase of K_{obs} value with pH could be quantified by plotting log K_{obs} *vs* pH, which gave the equation

$$\log K_{obs} = 0.19 \cdot pH - 2.5$$

for acetate buffers. At 30 °C, for similar pH values in inorganic buffers,[2] the equation was

$$\log K_{obs} = 2.8 \times 10^{-4} \cdot pH + 0.001.$$

The small value of the slope in the inorganic buffers proved the absence of catalysis due to excessively low pH, and K_{obs} could therefore be considered a constant. For acetate buffers, since pH = −log [H_3O^+] and

Table 1. Comparison of K_{obs}, E_a and $\Delta S^{\neq}$ values obtained with acetate and phosphate buffers at 22, 30 and 50 °C

Buffer	Composition (by volume)	pH	Temperature (°C)	K_{obs} ($h^{-1} \times 10^3$)	E_a (kJ mol^{-1})	$\Delta S^{\neq}$ (J mol^{-1} K^{-1})
$CH_3COOH + CH_3COONa$	61 + 39	4.4	22	7	85.0	−7
			30	16.7		
			50	141.4		
$CH_3COOH + CH_3COONa$	21 + 79	5.2	22	8.3	85.7	−2
			30	22.4		
			50	172.1		
$KH_2PO_4 + Na_2HPO_4$	98 + 2	5.2	22	1.6	67.8	−69
			30	2.6		
			50	20.0		

$[OH^-][H_3O^+] = k_E = 10^{-13.83}$ mol^2 litre^{-2} at 30 °C, K_{obs} could be expressed as a function of hydroxide ion concentration:

$$\text{if } \log K_{obs} = a \cdot \text{pH} + b, \quad \text{then}$$

$$K_{obs} = 10^{(b - a \cdot \log kE)} [OH^-]^a \qquad (3)$$

which gave $K_{obs} = 1.34 \cdot [OH^-]^{0.19}$ (for $a = 0.19$ and $b = -2.5$). In none of the buffers studied was the reaction found to be first order with respect to $[OH^-]$.

For any given temperature, the rate of the degradation of isoxaflutole depended on the nature of the buffer constituents and the pH (between pH 5.2 and pH 8.0 in phosphate buffer we found $\log K_{obs} = 0.51 \cdot$ pH -5.2). In general, the rate constant K_{obs} of the reaction can be written as follows:

$$K_{obs} = k_{H_2O} \cdot [H_2O] + k_{H_3O^+} \cdot [H_3O^+] + k_{OH^-} \cdot [OH^-]^a + k_{HA} \cdot [HA] + k_{A^-} \cdot [A^-] \qquad (4)$$

where the constituents of the buffer solution are HA and A^-, ie the acid and its conjugate base, respectively.[9] To simplify this equation, $k_{H_3O^+} \cdot [H_3O^+]$ can be expressed as a function of $[OH^-]$ and, because in dilute aqueous solutions the quantity of water can be considered as invariable, $[H_2O]$ can be included in the constant rate of the 'spontaneous' reaction: $k_{H_2O} \cdot [H_2O] = k_0$. The values of the catalytic constants k_{HA} and k_{A^-} can be calculated by fixing the ratio $r = [HA]/[A^-]$ (at constant pH) and eqn (4) becomes

$$K_{obs} = k_r + (k_{HA} + k_{A^-}/r)[HA].$$

For a given ratio r, K_{obs} against [HA] is a straight line and the separate values k_{HA} and k_{A^-} can be determined by comparing the slopes of two lines obtained for two different values of r. Thus, to determine whether the abiotic degradation of isoxaflutole into DKN was subject to general catalysis, and to calculate the values of the separate catalytic constants k_{HA} and k_{A^-}, the influences of phosphate and acetate concentrations were studied.

3.3 Influences of KH_2PO_4 and Na_2HPO_4 concentrations

The effect of increasing the concentration of phosphate anions was examined in aqueous solutions having initial isoxaflutole concentration of 10 mg litre^{-1} (at the same temperature; 30 °C). The degradation of isoxaflutole was followed in two solutions at pH 6.0 and in five solutions at pH 6.5. Results are given in Table 2.

At pH 6.0, $r = [HA]/[A^-] = 7.13$ and the equation was:

$$K_{obs} = 0.051\ [H_2PO_4^-] + 0.003,$$

and at pH 6.5, r was 1 and the equation was:

$$K_{obs} = 0.338\ [H_2PO_4^-] + 0.003.$$

Thus, the values of k for $H_2PO_4^-$ and HPO_4^{2-} were 0.0046 and 0.3331 litre mol^{-1} h^{-1}, respectively, and indicated that, in such a solution, the catalytic action of the acid $H_2PO_4^-$ was negligible in comparison with HPO_4^{2-}. The increase of K_{obs} with increasing concentration showed that the hydrolysis of isoxaflutole underwent general catalysis in the solutions investigated and the overall equation was:

$$K_{obs} = 0.0046\ [H_2PO_4^-] + 0.3331[HPO_4^{2-}] + 0.003.$$

Table 2. Influence of phosphate concentration on degradation of isoxaflutole in aqueous buffers at 30 °C and at pH 6.0 and 6.5

Concentration (M)			
KH_2PO_4	Na_2HPO_4	K_{obs}[a] ($h^{-1} \times 10^3$)	$t_{1/2}$[a] (h)
0.0585	0.0082[b]	5.9	116.6
0.1754	0.0246[b]	11.9	58.2
0.02	0.02[c]	10.0	72.0
0.05	0.05[c]	20 (±1)	35 (±2)
0.1	0.1[c]	37	18.7

[a] Mean of three replicate experiments.
[b] $r = [HA]/[A^-] = 7.13$ (pH 6.0).
[c] $r = [HA]/[A^-] = 1$ (pH 6.5).

3.4 Influence of CH_3COO^- concentration

The results given in Table 1 reveal a significant difference between rates of hydrolysis in phosphate and acetate buffers: at 30 °C and pH 5.2, the half-lives for phosphate and acetate were 267 and 31 h, respectively. Because it is known that under acidic conditions isoxazoles unsubstituted in the 3-position do not tend to open to give the corresponding β-ketone derivatives,[7,8] it was supposed that the greater rate of degradation in acetate buffer compared with phosphate buffer was due to the strong catalytic activity of the CH_3COO^- ion, the promoting action of which in reactions of nucleophilic elimination is already known.[10] In order to establish a relationship between K_{obs} and the CH_3COO^- concentration, the degradation of isoxaflutole was followed in phosphate buffers ($[KH_2PO_4] = [Na_2HPO_4] = 0.02$ M) to which different quantities of acetate anion were added, and then repeated with phosphate buffers containing KH_2PO_4 and Na_2HPO_4 at 0.05 M.

The initial isoxaflutole concentration was 10 mg litre^{-1}, the temperature of the experiments was 30 °C, μ was 0.2 M, and pH was 6.6 (±0.2). Results are given in Table 3.

Table 3. Catalytic action of acetate anion on the degradation of isoxaflutole in two aqueous phosphate buffers at 30 °C and at pH 6.6 (±0.2)

Sodium acetate	K_{obs} ($h^{-1} \times 10^3$)		$t_{1/2}$ (h)	
Concentration (M)	Buffer 1[a]	Buffer 2[b]	Buffer 1[a]	Buffer 2[b]
0.16	74	63	9.4	10.9
0.1	58	48	12.0	14.5
0.0	21	10	32.7	72.0

[a] $[KH_2PO_4] = [Na_2HPO_4] = 0.05$ M.
[b] $[KH_2PO_4] = [Na_2HPO_4] = 0.02$ M.

As for the phosphate buffers, the constant rate K_{obs} was found to be linearly dependent on the CH_3COO^- concentration (eqns (5a) and (5b)):

$$\text{for } [H_2PO_4^-] = [HPO_4^{2-}] = 0.02\text{M}, \quad K_{obs} = 0.3362[CH_3COO^-] + 0.0112 \qquad (5a)$$

$$\text{for } [H_2PO_4^-] = [HPO_4^{2-}] = 0.05\text{M}, \quad K_{obs} = 0.3352[CH_3COO^-] + 0.0219 \qquad (5b)$$

Taking the difference between the slopes to be due to experimental variation, an averaged slope of 0.3357 ($\pm 5 \times 10^{-4}$) litre mol^{-1} h^{-1} has been calculated. This represents the catalytic constant $k_{CH_3COO^-}$ of CH_3COO^- for isoxaflutole under the conditions previously described. The difference observed between the *y*-intercept and the value calculated from measurements in phosphate buffers without acetate anion (preceding paragraph) may be attributed to experimental errors and pH variation from one solution to another (from pH 6.4 to pH 6.8). As for the phosphate buffers (Table 2), the CH_3COOH and CH_3COO^- concentrations were increased in order to quantify the catalytic constant k_{CH_3COOH}. The values of K_{obs} obtained for pH 5.2 ($r = [CH_3COOH]/[CH_3COO^-] = 0.26$) and at 30 °C are given in Table 4.

The K_{obs} values obtained lead to a k_{CH_3COOH} value of 0.3085 litre mol^{-1} h^{-1}, which is similar to the value for $k_{CH_3COO^-}$ and allowed us to conclude that the catalytic actions of CH_3COOH and CH_3COO^- were equivalent. The overall equation was

$$K_{obs} = 0.3085 \cdot [CH_3COOH] + 0.3357 \cdot [CH_3COO^-] - 0.01.$$

Since the constant rate of the degradation of isoxaflutole into DKN in a [HA]/[A^-] buffer was a function of [HA] and [A^-], the velocity of the reaction could be supposed to be related to the capacity of the catalytic entity for approaching the isoxaflutole molecule. Because of the high number of water molecules that can hydrate HPO_4^{2-} (up to 12 water molecules),[11] the formation of the enolate ion could be hindered by the volume of the phosphate ion and this could explain the lower value of $\Delta S^{\neq}$ (Table 1) obtained in phosphate buffer.

Comparison of eqn (4) with eqns (5a) and (5b) indicates that the rate constant varied positively with increasing concentration for both organic and inorganic buffers studied, which meant that, regardless of the increased rate of degradation in aqueous solutions due to the catalytic action of the CH_3COO^- anion, it can be supposed that the degradation of isoxaflutole in water is subject to general catalysis in all types of buffer.

Table 4. Influence of concentration of components on K_{obs} values in acetate buffers at pH 5.2 and at 30 °C

Concentration (M)			
Acetic acid	Sodium salt	K_{obs} ($h^{-1} \times 10^3$)	$t_{1/2}$ (h)
0.021	0.079	22.4	30.9
0.042	0.158	55.4	12.5

3.5 Influence of R-substituent in RCOOH/RCOONa buffers

Because of the obvious action of CH_3COONa in the degradation of isoxaflutole in water, it seemed important to establish whether the same properties would be observed for other organic buffers. Since alkyl groups are electron-repelling, increasing their number in the α-position should lower the strength of the acid, and consequently increase the strength of its conjugate base. Dissociation of saturated dicarboxylic acids in water occurs in two steps. In the first ionisation, the acid loses a proton from two positions, but the corresponding ion formed can add a proton to only one position. This negatively charged carboxylate ion has an electrostatic effect which is assumed to require additional energy to separate the proton from the carboxyl group (field effect through the solvent). The carboxylate anion exerts an inductive effect (+I) with resultant weakening of the acid. In the second ionisation, the ion can lose a proton from only one position, but the di-anion can add a proton to two positions.[12] In order to evaluate the influence of the R-substituent in R-COOH/R-COONa buffers, the degradation of IFT was investigated at 30 °C in buffers consisting of the following acids and their sodium salts: propionic ($R = C_2H_5$), *n*-butyric ($R = C_3H_7$), isobutyric ($R = (CH_3)_2CH$) and trimethylacetic ($R = (CH_3)_3C$), and the dicarboxylic acid, succinic acid, and its conjugate base ($HOOCCH_2CH_2COOH$/$NaOOCH_2CH_2COONa$).

The similar pKa values of the above acid/base pairs allowed a constant pH value with the same proportion of acid and base for all the solutions (no influence of the anion concentration). To have pH = pKa, buffers were made with equal amounts of acid and base (by volume); the final concentrations of the acid and its conjugate base in solution were 0.05 M and the pH was 4.7 (±0.1). Results are given in Table 5.

The results obtained confirmed that methyl groups in the α-position increased the strength of the conjugate base $RCOO^-$, since we found $K_{obs}(CH_3) <$

Table 5. Influence of the nature of the R-substituent in alkanoic acid/sodium salt buffers at 30 °C and pH 4.7 (±0.1)

R-substituent	K_{obs} ($h^{-1} \times 10^3$)	$t_{1/2}$ (h)
CH_3	30	23.1
C_2H_5	44	16.0
C_3H_7	28	24.6
$(CH_3)_2CH$	39	17.8
$(CH_3)_3C$	49	14.1
Succinic acid[a]	22	31.6

[a] Data for an analogous succinic acid buffer included for comparison.

$K_{obs}((CH_3)_2CH) < K_{obs}((CH_3)_3C)$. We noticed that lengthening the carbon chain reduced the +I effect of the methyl group and slowed the reaction (the half-life obtained for $R=C_3H_7$ was higher than that obtained for $R=C_2H_5$). The value of the rate constant determined in a succinic acid/sodium succinate buffer allowed us to confirm that the absence of electron-repelling groups decreased the velocity of the reaction. By following the degradation of isoxaflutole in a succinic acid/sodium succinate buffer containing 0.033 M of each of these compounds ($K_{obs}=0.016\,h^{-1}$) it could be verified that the degradation of isoxaflutole in aqueous solutions is subject to general catalysis. Above all, the relevant point is that K_{obs} values of the same order of magnitude were obtained for the chemical degradation of isoxaflutole in buffers prepared with various organic acids and their conjugate bases. In all cases the K_{obs} values were at least ten times greater than those observed in phosphate buffer systems.

4 CONCLUSION

The experiments conducted at 30 °C in organic buffers confirmed that the degradation of isoxaflutole in aqueous solutions followed pseudo-first-order kinetics, was activated by temperature and catalysed in terms of the hydroxide ion concentration, as was previously found in inorganic buffers. The determination of the catalytic constants of $H_2PO_4^-$, HPO_4^{2-}, CH_3COOH and CH_3COO^- allowed us to propose that, in phosphate buffers, only the conjugate base participated in the reaction, whereas in certain organic buffers both the acid and its conjugate base took part in the degradation of isoxaflutole into the diketonitrile DKN. Thus, the influence of the nature and the concentration of the buffer reagents was significant, since it was possible to degrade isoxaflutole rapidly under acidic conditions in RCOOH/RCOONa buffers, whereas the compound could be considered to be almost stable in phosphate buffers at the same pH. Because organic acids (and their conjugate bases) are present in nature, the degradation of isoxaflutole into DKN may occur faster in reality than in the phosphate buffer model systems. Laboratory studies which aim at anticipating and understanding the behaviour of chemical products such as pesticides must take into account the composition of soil and groundwater before predicting the fate of xenobiotics in the natural environment. Since BA was not detected throughout this study, it can be supposed that the degradation of the diketonitrile DKN occurs in biologically active media only. Studies currently taking place with sterilised and unsterilised soils should confirm this point.

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