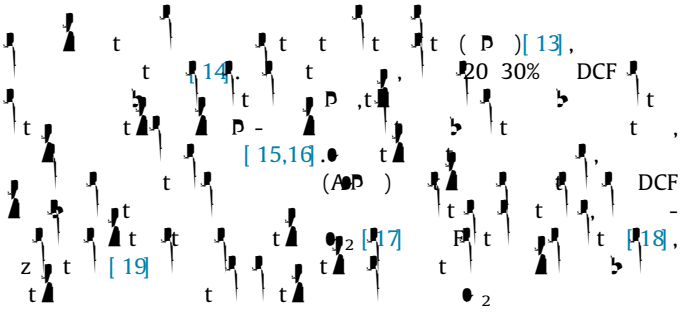


t t t Co 2 DCF. t t t -
t Co 2 t DCF t t :

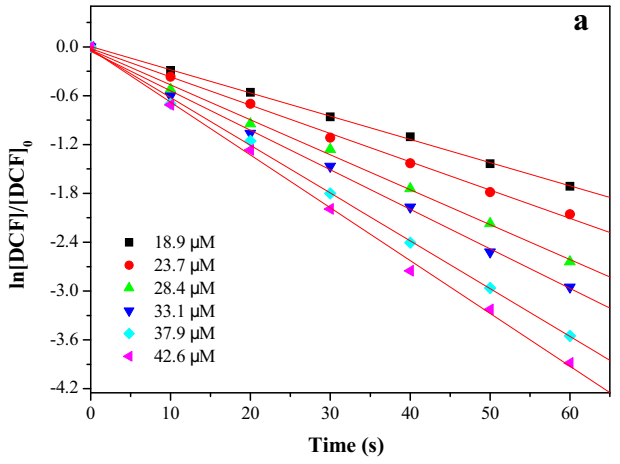
$$-\frac{[DCF]}{t} = k\,[DCF]^m[Co_2]^n \quad (1)$$

[Co] [DCF] t t t t Co 2 DCF, m
n t t t t t t t t -
t Co 2 DCF t , k t t t
t t . t t t
t Co 2 DCF (DCF] 0 = 3.00 μM,
[Co 2] 0 = 18.9 42.6 μM). t t Co 2 t t
18.9 μM t 42.6 μM, t t DCF
81.9% t 98.0% t 50 t t ,
t Co 2 t t t t t -
7.29%t 4.08% t 359
t t t t [33], t t t
Co 2 t t t t . E . (1) tt :

$$-\frac{[DCF]}{t} = k_3\,[DCF]^m \quad (2)$$

$$k_3 = k\,[Co_2]^n \quad (3)$$

DCF t t tt t
t t, t Co 2 (18.9 μM)
t t F . 1 , t t t t t t -



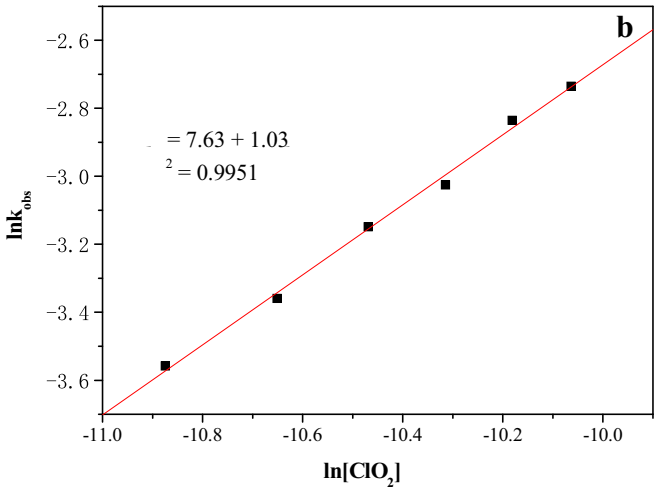


Fig. 1. D t t t t DCF t Co 2 ( ) t
(DCF] / [DCF] 0) t t t t t t Co 2 t t ;)
t (k) . [Co 2] 0 [DCF] 0 = 3.00 μM, = 7.0, T = 298 .

t t t t t DCF, . ., m = 1. D t
t - t t t (k_3, $^{-1}$) t
t t - t (DCF] / [DCF] 0)
t t t t Co 2.
F t t t t t DCF (3.00 μM), k_3
t Co 2 t t 18.9 μM t
42.6 μM (F). t k_3 . [Co 2] 0
(R^2 = 0.9951) 1.03 (0.032) (F)
t t t t t t - t
t t t Co 2 t t , . ., n = 1. z ,t -
t t DCF Co 2
- t t :

$$-\frac{[DCF]}{t} = k\,[DCF][Co_2] \quad (4)$$

F t (t t t t t
Co 2), k t E . (3).
k t t 1.51(0.017) × 10^3 M^{-1} $^{-1}$ t
Co 2 t t 18.9 μM, tt t t t
(k 1.05 × 10^4 M^{-1} $^{-1}$) t , t . [37] . , t
t 10^3 t t t (k = 3.89
1.17 M^{-1} $^{-1}$ t 7.0) [38] - DCF
t Co 2t t t 24.3(0.27)
50% DCF t t -
t t 1 $^{-1}$ 215 . t t
176- t t (k = 1.8 × 10^6 M^{-1} $^{-1}$), t t
t t z (k = 7.9 × 10^3 M^{-1} $^{-1}$) [7]
t - t t t
(k = 1.26 × 10^6 M^{-1} $^{-1}$) [10] t
tt Co 2. C t , (k < 0.1 M^{-1} $^{-1}$),
t (k ≈ 1 M^{-1} $^{-1}$) [39]
(k = 7.9 M^{-1} $^{-1}$) [9] t t t t
- t t .

3.2. Effect of pH on DCF oxidation

t t t t -
k t t t 298 . F . 2 t t t t
t DCF (3.00 μM) Co 2 (18.9 μM) t -
t . F 5.0 t 10.0, k_3 t
1.75(0.036) × 10^{-2} $^{-1}$ t 2.78(0.054) × 10^{-2} $^{-1}$ -
t t 2.78(0.054) × 10^{-2} $^{-1}$ t
1.94(0.035) × 10^{-2} $^{-1}$ t t t
2.78(0.054) × 10^{-2} $^{-1}$ t 7.0. A t k_3 t t tt

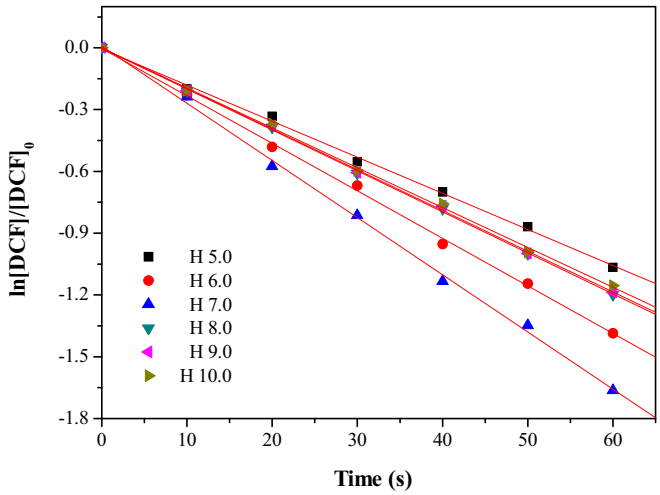


Fig. 2. D t [DCF] / [DCF] 0 . t t t t t .
[DCF] 0 = 3.00 μM, [Co 2] 0 = 18.9 μM, = 7.0, T = 298 .

Table 1
t t t t DCF t .

E . (3), t k DCF t C 2 -
t . A 1, -
k t ~1.12(0.016) × 10^3 M^-1 -1 h t
~2.13(0.032) × 10^-2 -1 t t t , t
tt t t t t t C , t -
t , t t t t t .
, t t t t t t t t t t DCF
C 2. t t DCF C 2 t t
t E . (5) (6):

DCF ⇌ DCF^- + + $K_a = 4.2$ [37] (5)

C 2 $\xrightarrow{+e^-}$ C 2^- $\xrightarrow{+2e^-}$ C ^- $\xrightarrow{+2e^-}$ C ^- [33] (6)

K_a C 2 1.96 K_a C 7.5 t 298 . F
5.0 t 7.0, DCF^-, C 2, C 2^- C t j -
t t t t t K_a . A C t -
t t C 2^- C ^- [33], t t t t t
t t DCF t t t t DCF
C t t . A 7.0, t t t
, t 7.0 t 10.0,
t t t DCF^- C , t
t t t t C ^- DCF^- .
A t t t C 2, t t t t -
t t t t t
t [40,41] . , t ,
t t t t C 2 t t
t t t [10], t t [11] t [42]
t . , t t t t
t t C 2 t t t t .

3.3. Effect of temperature on DCF oxidation

t DCF t t t t
k DCF t t t C 2
1.24(0.022) × 10^3 t 1.72(0.028) × 10^3 M^-1 -1 t t
t t 278 t 308 , t F . 3 (t).
A t t A t :

$$k = A - \frac{E_a}{RT} \quad (7)$$

E_a t t , R t
t t A - t t t .
D tt ( ) 1/T t t
t t t t t t t t -
t (T), F . 3. E_a t t t
7.87(0.14) -1 tt E . (7) t t t t .
t - E_a t t t
t t t t
t t t . t (ΔH^{++})
t (ΔS^{++}) t t t t t t
t t 5.38(0.17) -1 −165.75(3.03)
-1 -1, tt t t t - t
t t t t E E . [43]:

$$\frac{k}{T} = -\frac{\Delta H^{++}}{R} \times \frac{1}{T} + \frac{k_B}{h} + \frac{\Delta S^{++}}{R} \quad (8)$$

k_B B t z , t t h D t t .
E_a, ΔH t t
t t t t t t t t t t t -
t t t t t C 2 DCF, t t t
t t tt C 2. t t t t
t t DCF t t DCF
(DCF·).

3.4. Effect of oxygen concentration on DCF oxidation

D t t t t t t
t t t t t t t DCF,
t t t , . ., 2 2 -
(200 -1), t t :
A F . 4, t t t t t t, t
t t t t . tt t t t t (k_{obs})
2.63(0.058) × 10^-2 3.51(0.067) × 10^-2 2.84(0.051)
× 10^-2 -1 t 2 t t -
, t . t t t t
t t t DCF. , t t t
DCF t t t
t t t t t ( ),
, 2 2^-.

3.5. Kinetics model and mechanism for DCF oxidation

t t t t t t
DCF t C 2, t

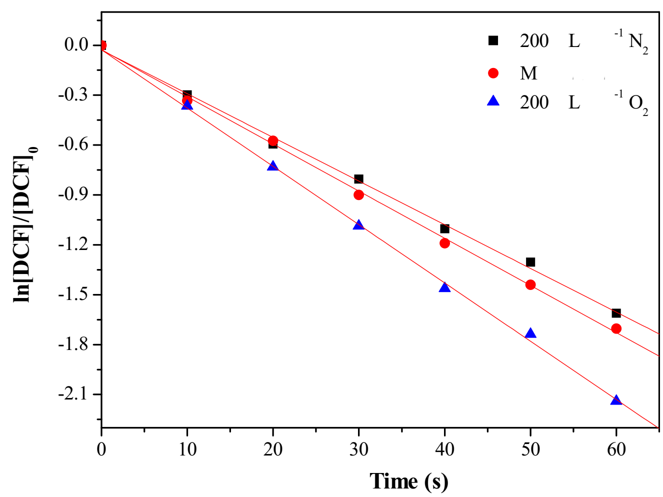


Fig. 4. t DCF t C● $_2$ t t t . [DCF]$_0$ = 3.00 μM, [C●$_2$]$_0$

[44] [18] . F . 5 ● $_2^{-}$ C● $_2$- DCF 7.0 t 298 . t DCF, . E t t t ● $_2^{-}$ ● A [45], t ● ● $_2^{-}$ t DCF :

$$R_{●} = \frac{k_{●}}{k} \approx \frac{k - k}{k} \quad (9)$$

$$R_{●_2^{-}} = \frac{k_{●_2^{-}}}{k} \approx \frac{k - k}{k} \quad (10)$$

$R_●$ $R_{●_2^-}$ t DCF ● ● $_2^-$, ; $k_●$ $k_{●_2^-}$ t ; k k ; k DCF t C● $_2$

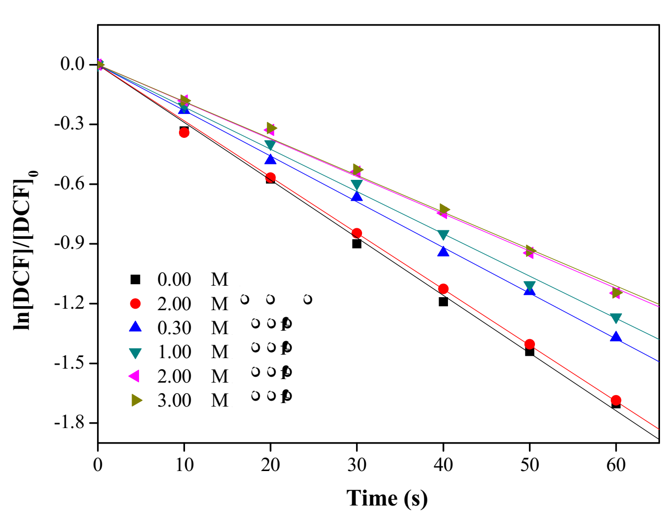


Fig. 5. E t t DCF (3.00 μM) t C● $_2$ (18.9 μM) t 7.0 298 .

2.73(0.14)%, $R_{●_2^-}$ 36.07(0.36)%. C t t t $R_●$ t DCF C● $_2$ t t DCF t ● $_2^-$ B (C● $_2$) [42] t t t t ● $_2^-$ DCF:

$$DCF + C●_2 \xrightarrow{k_1} DCF^{\cdot} + C●_2^{-} \quad (11)$$

$$DCF^{\cdot} + ●_2 \xrightarrow{k_2} DCF^{+} + ●_2^{-} \quad (12)$$

$$●_2^{-} \xrightarrow{k_3} ●_2 \quad (13)$$

$$●_2^{-} + DCF \xrightarrow{k_4} t \quad (14)$$

$$DCF^{\cdot} + C●_2 \xrightarrow{k_5} t \quad (15)$$

t k_1 t t DCF z tt t C● $_2$ t DCF$^{\cdot}$ C● $_2$, k_2 t DCF$^{\cdot}$ ● $_2$, k_3 t ●$_2^-$, k_4 t t ● $_2^-$ DCF, k_5 DCF$^{\cdot}$ C● $_2$. t (14) t t ● $_2^-$; t (15) t C● $_2$. ● $_2^-$, t (E . (4)) C tt :

$$-\frac{[DCF]}{t} = k_1[DCF][C●_2] + k_4[DCF][●_2^{-}] \quad (16)$$

t -t t t DCF$^{\cdot}$:

$$\frac{[DCF^{\cdot}]}{t} = k_1[DCF][C●_2] - k_2[DCF^{\cdot}][●_2] - k_5[DCF^{\cdot}][C●_2] = 0 \quad (17)$$

E . (17) :

$$[DCF^{\cdot}] = \frac{k_1[DCF][C●_2]}{k_2[●_2] + k_5[C●_2]} \quad (18)$$

t -t t t ● $_2^-$:

$$\frac{[●_2^{-}]}{t} = k_2[DCF^{\cdot}][●_2] - k_3[●_2^{-}] - k_4[DCF][●_2^{-}] = 0 \quad (19)$$

E . (19) :

$$[●_2^{-}] = \frac{k_2[DCF^{\cdot}][●_2]}{k_3 + k_4[DCF]} \quad (20)$$

t t t E . (18) (20) t E . (16) :

$$-\frac{[DCF]}{t} = \frac{k_1k_2k_4[●_2][C●_2]}{(k_2[●_2] + k_5[C●_2])(k_3 + k_4[DCF])}[DCF]^2 + k_1[DCF][C●_2] \quad (21)$$

E . (21) :

$$k = -\frac{[DCF]}{t[DCF]} = \frac{k_1k_2k_4[●_2][C●_2]}{(k_2[●_2] + k_5[C●_2])(k_3 + k_4[DCF])}[DCF] + k_1[C●_2] \quad (22)$$

A t E . (22), t t [DCF]$_0$ t k . F . 6 t t DCF t t k, t y t t k t t C● $_2$. t DCF t t

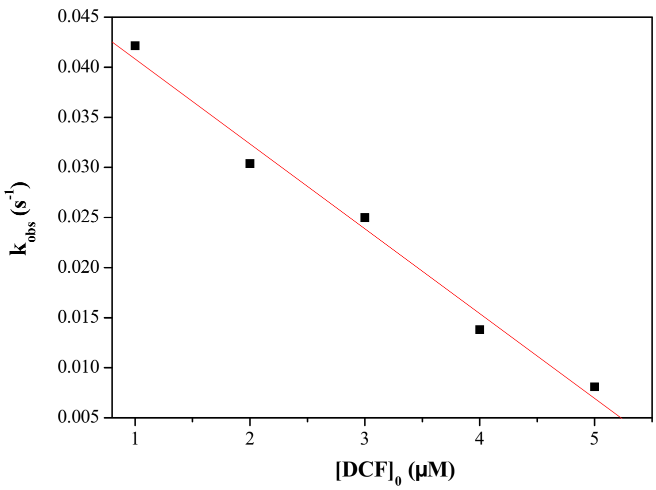


Fig. 6. k_{obs} ... DCF ... CO_2 (18.9 μM) ... DCF ... (1.00 5.00 μM) ... 7.0 ... 298 .

... $4.21(\ 0.13) \times 10^{-2}$, $3.04(\ 0.085) \times 10^{-2}$, $2.50(\ 0.054) \times 10^{-2}$, $1.38(\ 0.039) \times 10^{-2}$ $8.09(\ 0.21) \times 10^{-3}$ $^{-1}$ ... DCF ... 1.00, 2.00, 3.00, 4.00 5.00 μM, ... F ... Fig. 6, ... k_{obs} ... $[DCF]_0 = 0$, ... k_{obs} ... k ... $4.96(\ 0.018) \times 10^{-2}$ $^{-1}$ ... $2.61(\ 0.094) \times 10^3$ M^{-1} $^{-1}$, ...

A ... DCF ... DCF ... CO_2 ... (1): (1) ... DCF ... CO_2 ... DCF ... CO_2^-. (2) D ... DCF ... CO_2, ... CO, ... CO, ... G [33]. ... [31,46]:

$$DCF^{\cdot} + CO_2 \rightarrow DCF - O + CO \quad (23)$$

$$DCF^{\cdot} + CO_2 \rightarrow \quad - DCF + CO \quad (24)$$

$$DCF^{\cdot} + \ ^{+} + CO \rightarrow DCF^{+} + \ C \quad (25)$$

$$DCF^{\cdot} + \ C \rightarrow DCF - C + \ _2 \quad (26)$$

... -DCF, ... -DCF ... -DCF ... [29], ... (3) $DCF^{\cdot}$ ... O_2^- ... (4) DCF ... O_2^- ... G ... CO_2 ... O_2^- ... DCF ... .

4. Conclusions

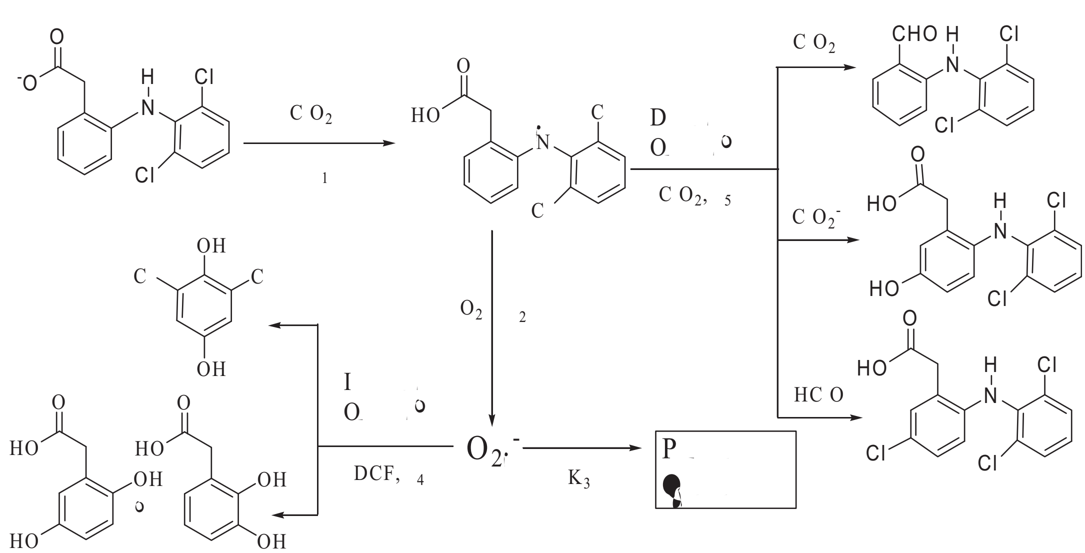
... DCF ... CO_2 ... :

(1) DCF ... CO_2. A ... k ...

(2) ... k ... $1.51(\ 0.017) \times 10^3$ ... 7.0. ... $7.87(\ 0.14)$ $^{-1}$, ... $5.38(\ 0.17)$ $^{-1}$ ... $-165.75(\ 3.03)$ $^{-1}$ $^{-1}$, ...

(3) ... DCF ... (36.07%) ... O_2^- ... ( ) ... ( ), ... DCF ... O_2^- ...

(4) ... DCF ... CO_2 ... : ... CO_2 ... O_2^-.



Scheme 1. ... DCF ... CO_2.

Acknowledgments

F t C (. 21377031, 81401470), t t
p j t G p (. 2013B020800009),
t t F t p (.
132300410158, 112300410104); t p j t E t D t t p
(. 13A610516, 13A610853).

References

[1] A. , . , . , . , C t t t
t t , z .
M t . 276 (2014) 499 509.
[2] . G. G , AD t z, A. t , t t t
t t t , D .
C . A 118 (2014) 1293 1299.
[3] . E , AD . . t , .B B t , F. , A t t t
t t *E. faecalis* ,
. E . 31 (2005) 672 675.
[4] M. . M. , G. , D t t
, t . 44 (2010) 3243 3251.
[5] . , F. B t , . -G t , . M , . , P . ,
G , C. , .-C. t , M.D t t -C , / B -CD M/
B t t t t : t t t
t , B . 121 (2012) 68 75.
[6] G , . G , A , . C , . . A , t
t t t t t , C .
E . 185-186 (2012) 230 242.
[7] M.M. , . , .A. , G t , t
t t t t t , t .
39 (2009) 3607 3617.
[8] . , M. A , . G , t t t
t t t : t t t t t t t t
t , t . 42 (2008) 1935 1942.
[9] D . , . . , C. , t : t t ,
t t t t , t . 44 (2010) 5989 5998.
[10] D . , . . , C , t t t t t
t , t . 45 (2011) 1838 1846.
[11] F. , .MQ , C. , . , . D , t
t t t ,
C . 79 (2010) 646 651.
[12] A.B t , F. C t , .B. , t
t t t t t t :
t t , B . . 98 (2007) 2359 2385.
[13] A. , .D. t , D t t t t
t t t t , . t E . 397 (2008) 148 157.
[14] .M z, .C. z-D , M. t , M. , . B , A. G z , A.
G , . G , M. . . A , A.M. . t , D. B ,
B t t
t t t t (t t), E . .
C . 28 (2009) 2706 2714.
[15] . z, M. C , F. , .M. , t
t DD) t t ?,
E . . B t . 7 (2008) 125 138.
[16] D z, D. B , A t C-M t t t t t
t t t t t t , AC A .
C . 27 (2008) 836 846.
[17] . M -G , . z, B. z, .M. C , . M , M .
M , D t t t t t t t
t t t t t t z 2
t t, A . C t . B 105 (2011) 294 301.
[18] . B , D. , . , D t t t z F t
t , A . C t . B 134 135 (2013) 93 102.
[19] A. A , F. B t , .F. G -A , A. , D t t
z t t t t t : t
, C E . 189 (2012) 275 282.
[20] . M , A. A D. . , D z, MD t , D.
B , D. F tt - D t t t t t
t t t
( ) t t , A . C t . B 147 (2014) 1015 1027.
[21] . M , D . . . , . A , M. , F. G , M. A ,
t t t t t
t, C 80 (2010) 747 752.
[22] . P z, M. C , . , . , M. , . . ,
. t t , D t ,
E . . . 44 (2010) 3449 3454.
[23] . , t t t
t , . . 266 (2002) 175 189.
[24] D. t t , . . M. t, M t , .
t t t t , t , . t E . 405 (2008) 310
316.
[25] M.A t , . C t t , D. D , C. , D. D , .E. G , . t ,
. t z, A.A. C , A.A. M , D t
t t G t t (147, 60,
2007), E D t . 149 (2007) (2007). 252-252.
[26] . C , A. . E , . . , . :D t .
t t t t t t t t
C t , , t t t t
( ), A t . 68 (2004) 151 166.
[27] M.D. , M. M z , A. . F z , D. B E t
t t t t t t ,
t t , t 69 (2006) 334 342.
[28] C M.D D t t E D t t
C D t 2000/60/EC 2008/105/EC t
t t t (31.01.2012), 2011, . 876.
[29] . , . G. , . , t t
: t t t j t t t t t
t , t E . 473 474 (2014) 437 445.
[30] A . t , . t t t t t
t t , D . C . A 102 (1998) 7267 7272.
[31] C , D.M. t , t t t t t t
t t , D . C . A 118 (2014) 6827 6831.
[32] . . D , .F. , t t t t 2- t -4,6-
t (D) t t C 2 t
t t , . z . M t . 183 (2010) 347 352.
[33] A. , . . , D. . M , t
t t t t t , . C . 45
(2006) 8768 8775.
[34] D . . , . j M. . , D . B , A . M ,
t t t t t t t t -
: t tt , E . . . 40 (2006)
1504 1510.
[35] M. t , D. . t t , D. . M , C t
5′- , C . . 19 (2006) 1451 1458.
[36] D. t t , M. t t E . B t -A t , D. . M ,
t t t t ,
C . 47 (2008) 1639 1647.
[37] M.M. , . C , G. , D , . G t , t
t t z t t ,
E . . 37 (2003) 1016 1024.
[38] M. , M. D , B. , A t t : t
t t t t t t t t , t . 46 (2012) 3377
3386.
[39] . , . G t , t t t t t
t t t t t t : t t
(, t ( ), z) - t t
( ), t . 44 (2010) 555 566.
[40] A. . t , . , E t , t t
t t t t t , D . C . A 107 (2003) 10063 10068.
[41] G. C ″, A. . t t t
t t t t , D . C . A 16 (2012) 2911 2919.
[42] . , . , B , C - t t
t t z t , D . C . A 115 (2011) 11682 11688.
[43] . , M. M t , . A B t , M. . , A. t , . . t t ,
, E . . . 43 (2009) 509 515.
[44] . C C. , . Q , M. , t t t t t
t t t t t t t
t t , D t D . A 197 (2008) 81 87.
[45] A. . B , B. . E , B. C , . M , t t t t
: t t t t t t t
t t t D M , E . . . 42
(2008) 5492 5498.
[46] A . t , . , t t t t
, D . C . A 110 (2006)
4753 4758.