Electronic Supporting Information (ESI) for the paper:

Crossed molecular beam experiments and theoretical simulations on the multichannel reaction of toluene with atomic oxygen

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S1. Crossed-beam experimental details for O(^{3}P,^{1}D) + toluene: the effect of *soft* ionization

S2. Derivation of the product Branching Fractions (BFs)

S1. Crossed-beam experimental details for O(^{3}P,^{1}D) + toluene: the effect of *soft* ionization

As discussed in the main text, product angular and time-of-flight (TOF) distributions were measured using soft electron ionization (EI) (at 17 eV rather than hard ionization at 70 eV, because soft EI permits to mitigate and even suppress the interferences coming from dissociative ionization of reactant beams, products, and background gases. The use of *soft* ionization was critical for disentangling the reactive signal at $m/z = 65$, because toluene fragments strongly to $m/z = 65$ upon electron impact at 70 V, while negligibly at 17 eV. This is well illustrated in Fig. S1, which shows product TOF spectra at $m/z = 65$ for two different LAB angles using 70 eV and 17 eV. As can be seen, using 17 eV it is possible to measure in a clean manner the co-product(s) C_6H_5O ($m/z = 93$) of CH_3 at its (−28) daughter ion $m/z = 65$ (CH_3 elimination channel(s) 2a/2b)), having suppressed the otherwise (at 70 eV) overwhelming contributions from elastically/inelastically scattered toluene from the oxygen seeded beam.
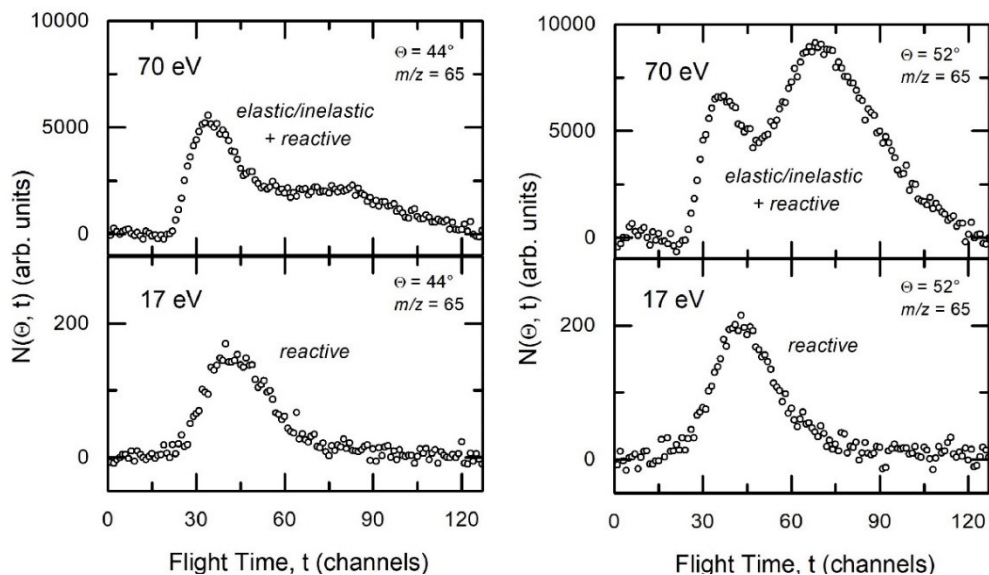

Fig. S1 TOF distributions, N(Θ,t), for $m/z = 65$ at Θ = 44° (*lhs*) and Θ = 52° (*rhs*) for the O(^{3}P,^{1}D) + toluene reactions (E$_c$ = 34.7 kJ/mol), employing *hard* (70 eV) (top panels) and *soft* (17 eV) (bottom panels) electron ionization. Signals at 70 eV reflect dominantly elastic/inelastic scattering of toluene from the seeded oxygen beam, with the reactive signal being minor and buried under the much stronger elastic/inelastic components. Signals at 17 eV (which are a factor 50 lower than at 70 eV) are only reactive signal, since elastic/inelastic contributions from dissociative ionization of toluene are suppressed. The angular and TOF distributions at $m/z = 65$ reported in Fig. 3 (bottom panel) and Fig. 4c of the main text were measured using 17 eV electrons, and they reflect only the reactive contributions. We stress that in the only previous CMB study of the O(3P) + toluene reaction,[1] the measurements were performed using 200 eV electron energy and, consequently information on the CH_3 elimination channel was much more difficult to extract.

S2. Derivation of the product Branching Fractions (BFs)

A most useful information on the dynamics of a multichannel reaction is the branching fraction (BF) of the various channels. Knowledge of the product BFs, besides its fundamental relevance, is of high interest for the modeling of systems of practical interest, such as combustion systems and astrochemical environments. To estimate the BFs from CMB experiments we need to know (*i*) the absolute beam intensities, (*ii*) the exact size of the collision volume, and (*iii*) the detection efficiency. Unfortunately, these quantities are not easy to determine accurately in a CMB experiment. However, since the first two are constant and the third can be reasonably estimated, we can readily determine relative reactive cross sections. In fact, it is possible to obtain the ratios between the yields of the various product channels starting from their apparent cross sections (*i.e.*, the relative weights w_i in the equation $I_{CM}(\theta, E'_T)_{total} = \Sigma_i\, w_i \times [T(\theta) \times P(E'_T)]_i$ used in the best-fit analysis (see section 2.1 in the main text). We have followed the procedure initially outlined by Schmoltner *et al.*[2] and have taken advantage of the soft EI approach for deriving, over the years, the product BFs of a variety of polyatomic multichannel reactions, in particular those of atomic oxygen with aliphatic unsaturated hydrocarbons (UHs)[3-17] as well as with aromatics.[18,19] pyridine,[20] and unsaturated nitriles.[21,22] As discussed in ref. (IRPC 2015), let suppose that the reaction has only two competing product channels, as in $O(^3P) + C_2H_2$,[10] and let us call the two corresponding products *A* and *B*. From the laboratory angular and TOF distributions of the reaction products *A* and *B* and from the fitting procedure one obtains the apparent total cross sections for *A* and *B* formation, $\sigma^0(A)$ and $\sigma^0(B)$ (whose ratio is equal to the ratio of the w_A and w_B weights - see above). By correcting the apparent cross sections $\sigma^0(A)$ and $\sigma^0(B)$ for the ionization cross sections of *A* and *B*, $\sigma_{ion}(A)$ and $\sigma_{ion}(B)$, the fragmentation patterns of A and B, and the quadrupole mass filter transmission, one obtains the relative reaction cross sections, $\sigma(A)$ and $\sigma(B)$. We can therefore calculate the ratio between the relative reactive cross sections of the formation channels of the two generic products *A* and *B* from the relation:

$$\frac{\sigma(A)}{\sigma(B)} = \left(\frac{\sigma^0(A)}{\sigma^0(B)}\right) \times \left(\frac{\sigma_{ion}(B)}{\sigma_{ion}(A)}\right) \times \left(\frac{f(B \rightarrow m/z)}{f(A \rightarrow m/z)}\right)$$

where $f(A \rightarrow m/z)$ and $f(B \rightarrow m/z)$ are the fractions of *A* and *B* giving ions at that *m/z* ratio, corrected for the quadrupole transmission.

The σ_{ion} at their maximum (about 70 eV) are evaluated using the procedure of Fitch and Sauter,[23] which is based on the additivity of atomic ionization cross sections. The σ_{ion} are then scaled at the electron energy of 17 eV (which is the value usually used in our *soft* electron ionization method) using the total ionization cross section curves measured, when possible, at the parent mass of A and B, if these are stable, known molecules, as a function of electron energy. This is an approximation which seems to work well, because we are interested in the ratio of ionization cross sections and the ratio $\sigma_{ion}(A)/\sigma_{ion}(B)$ should be more accurate than the absolute values of $\sigma_{ion}(A)$ and $\sigma_{ion}(B)$ at 17 eV so determined (it turns out that the $\sigma_{ion}(A)/\sigma_{ion}(B)$ ratio at 17 eV is very similar to that at 70 eV, presumably because at 17 eV we are still well above the ionization threshold of all molecular/radical species). The estimate of the fragmentation spectrum of A and B is another important step in the procedure. This is determined by TOF measurements (at 17 eV electron energy) at the various possible fragment masses which can be detected. This works very well for the simplest case of two competing channels, as in the O(^{3}P) + C$_2$H$_2$ reaction;[10] for more complex cases, when more than two competing channels are present (and this is the case for most of the systems investigated), when some *m/z* cannot be explored, we rely on the fragmentation pattern of the stable molecule/radical or of a similar molecule. We are neglecting in this way the effect of the product internal excitation on the fragmentation pattern; but we do not expect this effect to be very large since the electron energy of 17 eV is well above the ionization threshold of organic molecules/radicals. The quadrupole transmission has been calibrated using a beam of stable molecules, whose fragmentation is known at 70 eV,[24] by determining the relative intensity of the various fragments under our detection conditions.

The branching fractions derived in this way have overall uncertainties which can range from ±25% to ±50% depending on the channel (see Table 1 in main text). The uncertainty of the overall procedure is attributable to three main reasons. The ionization cross sections have an uncertainty of about 20%, since for their determination we have employed an empirical procedure[23] whose applicability to polyatomic radicals has not been verified yet. Firstly, assuming that the overestimate of the σ_{ion} obtained following Fitch and Sauter[23] is similar for two different species, their ratio should be reliable to within 20-30%. Secondly, the fragmentation of the various product species has an uncertainty which can range from 20% to 40%. Finally, the apparent cross sections derived from the best-fit analysis of the experimental data have an accuracy of the order of 10-20%.

The above approach for deriving product BFs has revealed to be capable of providing experimental BFs for a variety of multichannel reactions that are in good or reasonable agreement with theoretical BFs derived from statistical calculations, using the Rice-Ramsperger-Kassel-Marcus/Master Equation (RRKM/ME) approach on *ab initio*, coupled triplet/singlet potential energy surfaces (PESs).[7,9,19]

REFERENCES

1   R. J. Baseman, R. J. Buss, P. Casavecchia and Y. T. Lee, *J. Am. Chem. Soc.*, 1984, **106**, 4108-4111.

2   A. M. Schmoltner, P. M. Chu and Y. T. Lee, *J. Chem. Phys.*, 1989, **91**, 5365-5373.

3   P. Casavecchia, G. Capozza, E. Segoloni, F. Leonori, N. Balucani and G. G. Volpi, *J. Phys. Chem. A*, 2005, **109**, 3527-3530.

4   P. Casavecchia, F. Leonori, N. Balucani, R. Petrucci, G. Capozza and E. Segoloni, *Phys. Chem. Chem. Phys.*, 2009, **11**, 46-65.

5   B. Fu, Y.-C. Han, J. M. Bowman, L. Angelucci, N. Balucani, F. Leonori and P. Casavecchia, *Proc. Natl. Acad. Sci. U.S.A*, 2012, **109**, 9733-9738.

6   P. Casavecchia, F. Leonori and N. Balucani, *Int. Rev. Phys. Chem.*, 2015, **34**, 161-204.

7   F. Leonori, N. Balucani, V. Nevrly, A. Bergeat, S. Falcinelli, G. Vanuzzo, P. Casavecchia and C. Cavalloti, *J. Phys. Chem. C*, 2015, **119**, 14632-14653.

8   A. Caracciolo, G. Vanuzzo, N. Balucani, D. Stranges, P. Casavecchia, L. Pratali Maffei and C. Cavallotti, *J. Phys. Chem. A*, 2019, **123**, 9934-9956.

9   C. Cavallotti, A. Della Libera, P. Recio, A. Caracciolo, N. Balucani and P. Casavecchia, *Faraday Discuss.*, 2022, **238**, 161–182.

10   F. Leonori, N. Balucani, G. Capozza, E. Segoloni, G. G. Volpi and P. Casavecchia, *Phys. Chem. Chem. Phys.*, 2014, **16**, 10008 – 10022.

11   N. Balucani, F. Leonori, P. Casavecchia, B. Fu and J.M. Bowman, *J. Phys. Chem. A*, 2015, **119**, 12498-12511

12   G. Vanuzzo, N. Balucani, F. Leonori, D. Stranges, V. Nevrly, S. Falcinelli, A. Bergeat, P. Casavecchia and C. Cavallotti, *J. Phys. Chem. A*, 2016, **120**, 4603-4618.

13   I. Gimondi, C. Cavallotti, G. Vanuzzo, N. Balucani and P. Casavecchia, *J. Phys. Chem. A* 2016, **120**, 4619-4633.

14   F. Leonori, A. Occhiogrosso, N. Balucani, A. Bucci, R. Petrucci and P. Casavecchia, *J. Phys. Chem. Lett.*, 2012, **3**, 75-80.

15   A. Caracciolo, G. Vanuzzo, N. Balucani, D. Stranges, P. Casavecchia, L. Pratali Maffei and C. Cavallotti, *J. Phys. Chem. A*, 2019, **123**, 9934-9956.

16   A. Caracciolo, G. Vanuzzo, N. Balucani, D. Stranges, S. Tanteri, C. Cavallotti and P. Casavecchia, *Chin. J. Chem. Phys.*, 2019, **32**, 113-122.

17   H. Pan, K. Liu, A Caracciolo and P. Casavecchia, *Chem. Soc. Rev.*, 2017, **46**, 7517-7547.

18   C. Cavallotti, C. De Falco, L. P. Maffei, A. Caracciolo, G. Vanuzzo, N. Balucani and P. Casavecchia, *J. Phys. Chem. Lett.*, 2020, **11**, 9621−9628.

19   G. Vanuzzo, A. Caracciolo, T. K. Minton, N. Balucani, P. Casavecchia, C. de Falco, A. Baggioli and C. Cavallotti, *J. Phys. Chem. A*, 2021, **125**, 8434-8453.

20   P. Recio, S. Alessandrini, G. Vanuzzo, G. Pannacci, A. Baggioli, D. Marchione, A. Caracciolo, V. J. Murray, P. Casavecchia, N. Balucani, C. Cavallotti, C. Puzzarini and V. Barone, *Nat. Chem.*, 2022, **14**, 1405-1412.

21   P. Liang, E. V. F. de Aragão, G. Pannacci, G. Vanuzzo, D. Marchione, P. Recio, D. Stranges, P. Casavecchia, N. Faginas Lago, L. Mancini, M. Rosi and N. Balucani, *J. Phys. Chem. A*, 2023, **127**, 685-703.

22   G. Pannacci, L. Mancini, G. Vanuzzo, P. Liang, D. Marchione, M. Rosi, P. Casavecchia and N. Balucani, *Phys. Chem. Chem. Phys.*, 2023, **25**, 20194-20211.

23   W. L. Fitch and A. D. Sauter, Anal. Chem. **55**, 832 (1983).

24   NIST Chemistry WebBook, 2002.