

Supporting Information for:
Investigating the thermal and photochemical reactions of ozone with
2,3-dimethyl-2-butene
Coleman and Ault

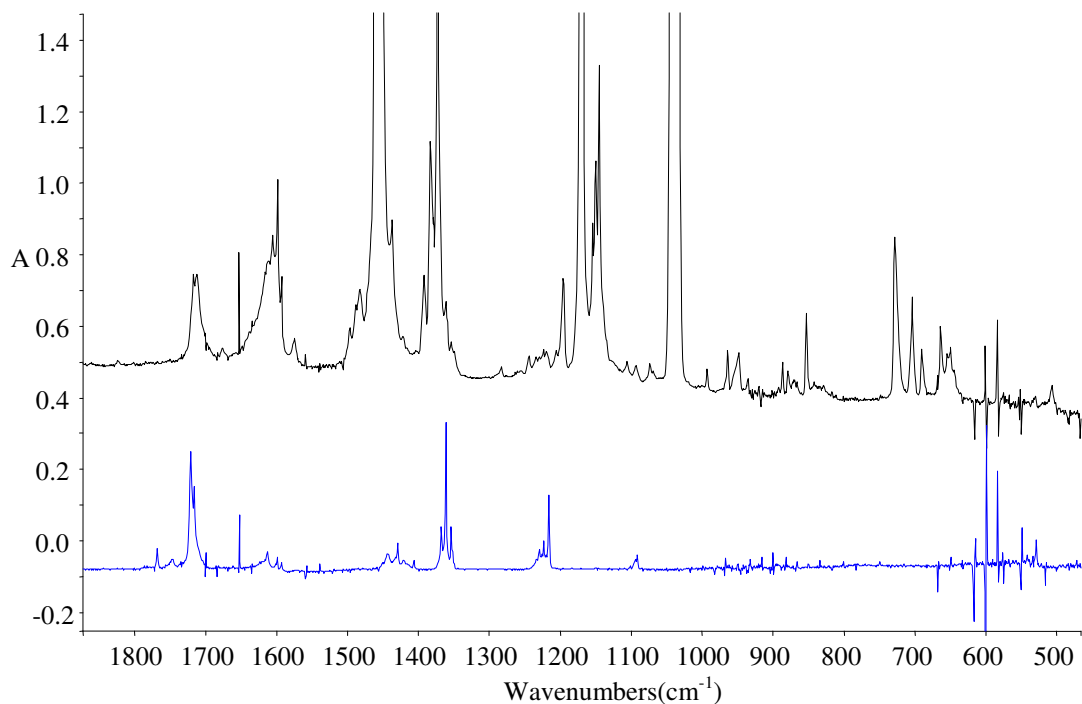


Figure S1. Black trace is the IR spectrum of twin jet deposited Ar:O₃:DMB = 500:1:1 annealed to 35K. Blue trace is IR spectrum of blank Ar:acetone = 250:1.

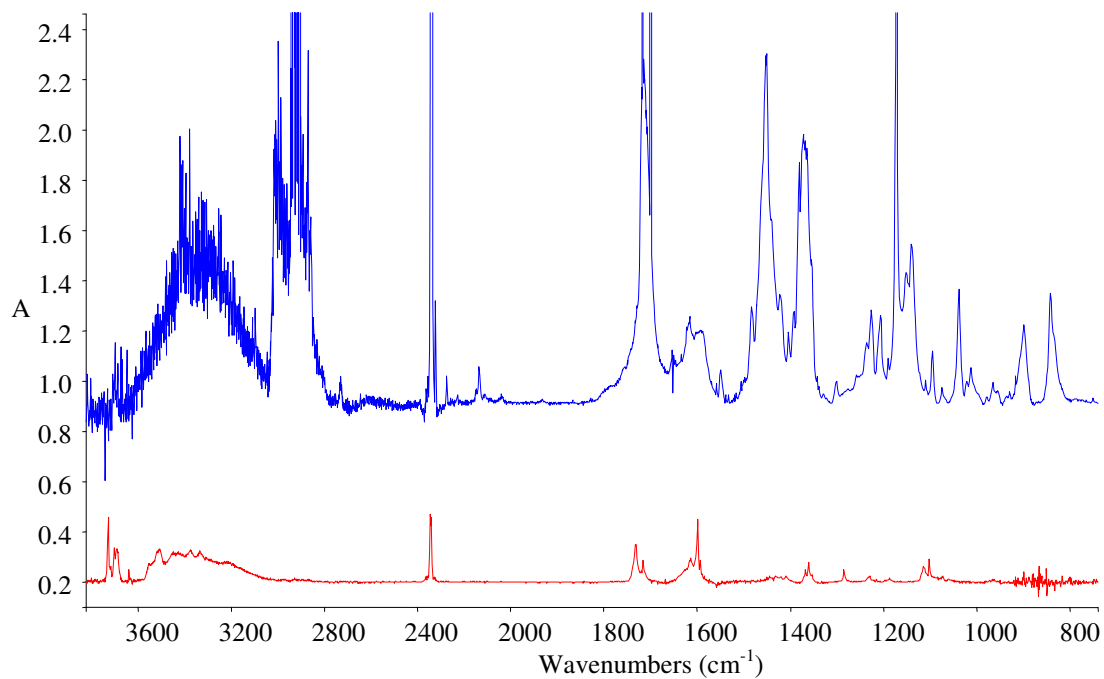


Figure S2. Blue trace is the IR spectrum of twin jet deposited O₂:DMB:O₃ = 500:1:1 irradiated at $\lambda \geq 220\text{nm}$. Red trace is IR spectrum of blank Ar: hydroxyacetone = 250:1.

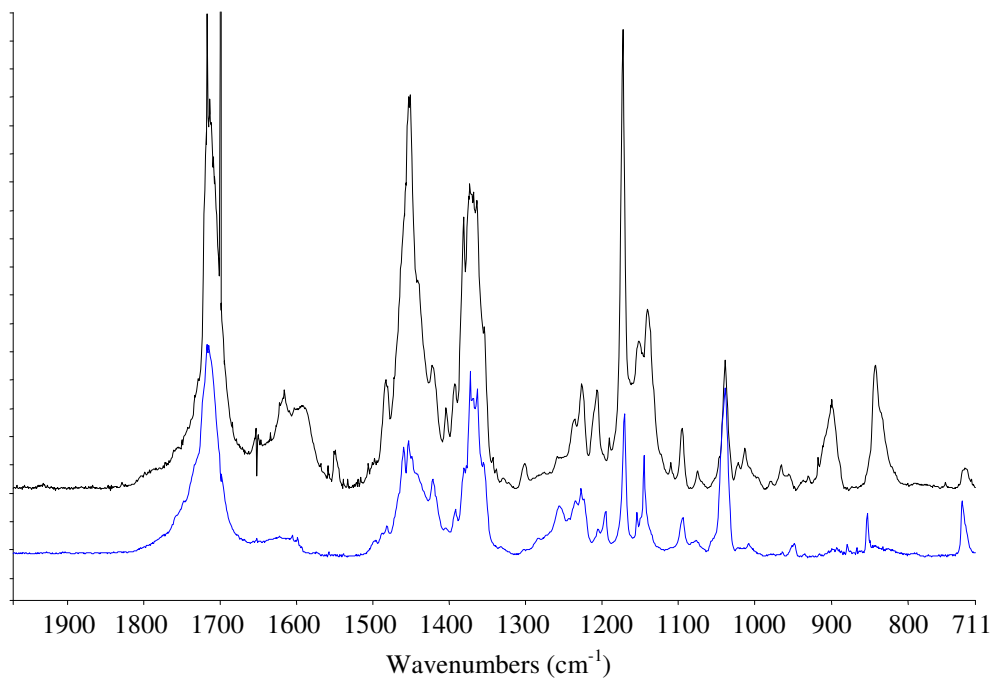


Figure S3. Blue trace is the IR spectra of twin jet deposited Ar: O₃:DMB =500:1:1 irradiated for 1 h with $\lambda \geq 220\text{nm}$. Black trace is the same experiment, however with O₂ used as the host gas.

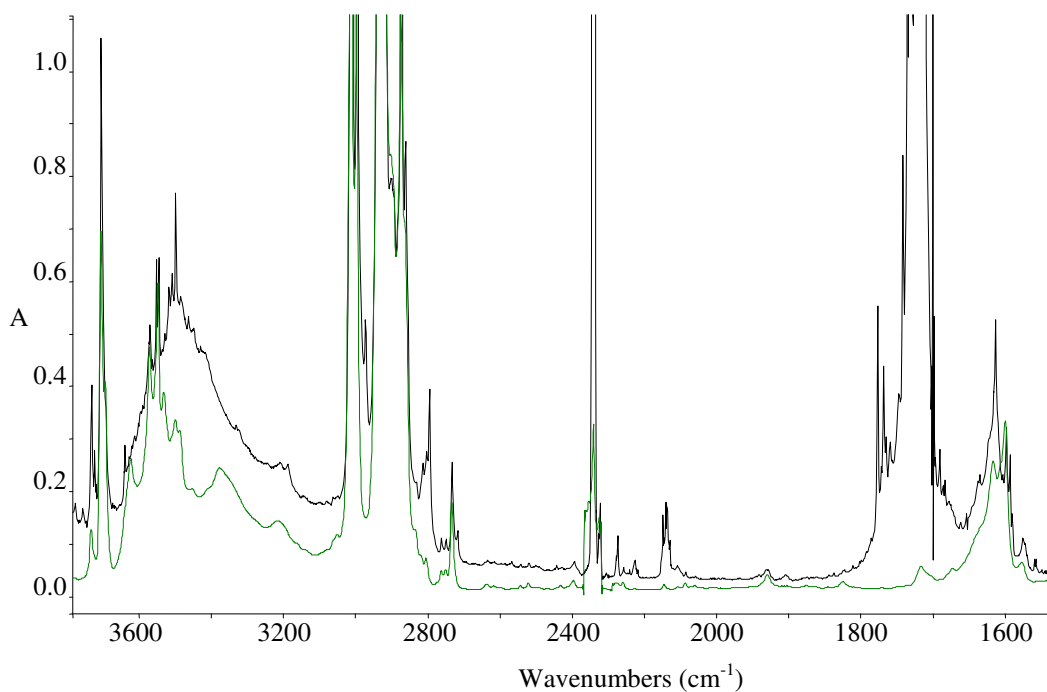


Figure S4. Black trace is the IR spectrum of merged jet (2m) Ar: O₃:DMB = 500:1:1. Below is Ar:DMB = 250:1.

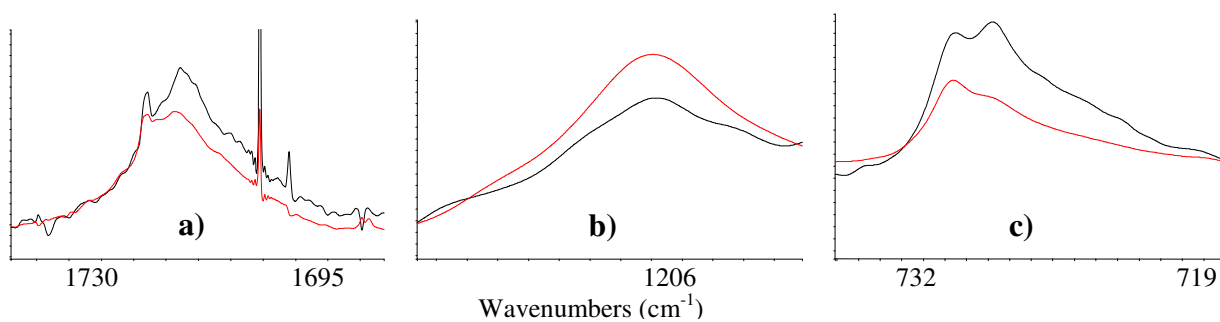


Figure S5. Representative IR spectra regions for **a)** acetone, **b)** secondary ozonide, and **c)** primary ozonide using the concentric jet mode with Ar: O₃:DMB = 500:1:1 in both red and black traces. Black trace is with $d = -1$ cm and red trace is with $d = -6$ cm. Intensities are **not** to scale (regions are enlarged to show detail).

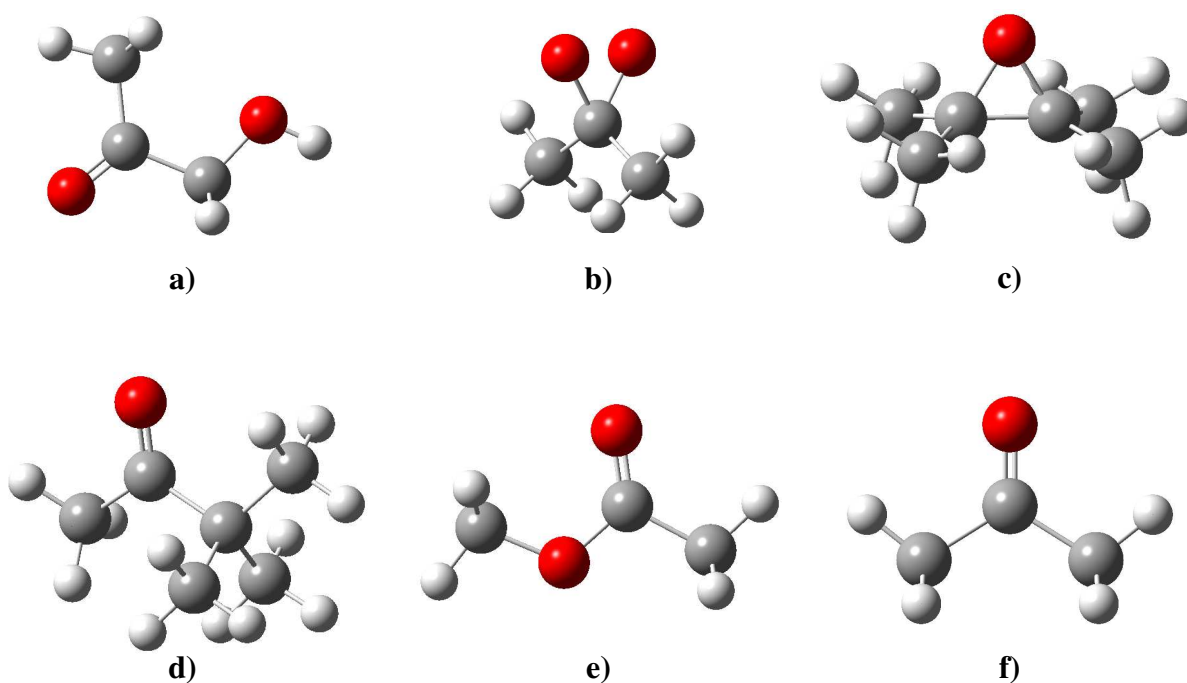


Figure S6: Calculated structures for **a)** hydroxyacetone, **b)** dimethyldioxirane, **c)** tetramethyloxirane, **d)** 3,3-dimethyl-2-butanone, **e)** methyl acetate, **f)** acetone.

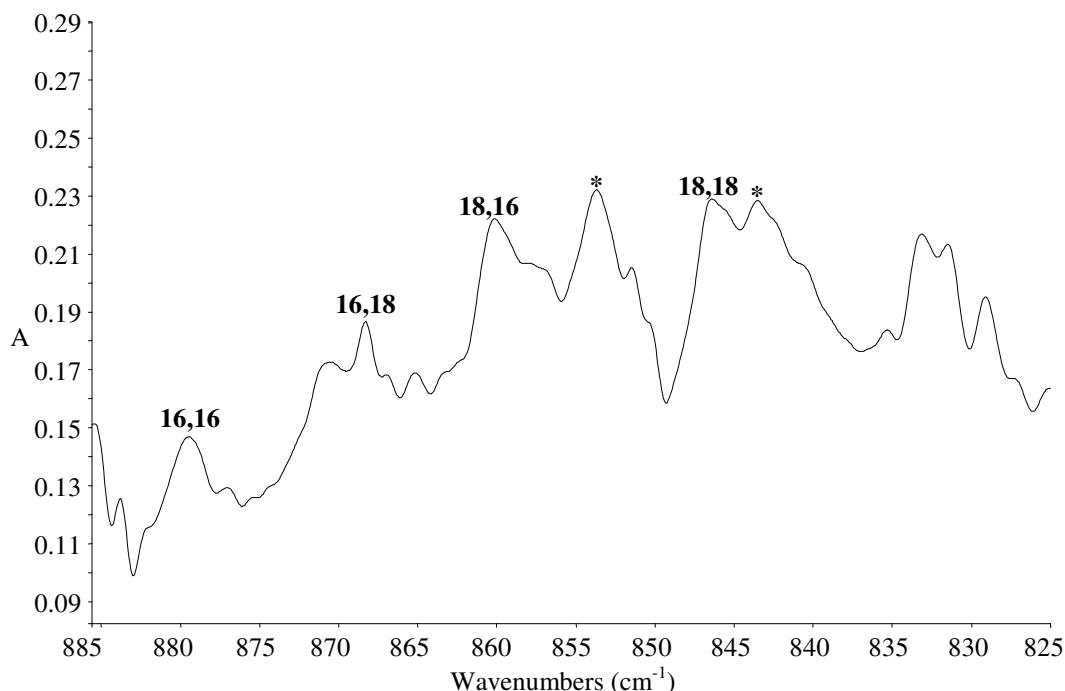


Figure S7. Infrared spectrum from 825 to 885 cm^{-1} arising from the twin jet deposited Ar:DMB = 250 with a sample of Ar: $^{16,18}\text{O}_3$ = 250. The features noted with an asterisk (*) are of the primary ozonide isotopomers. Labeled bands are assigned to the Criegee intermediate isotopomers.

Table S1. Product Intensities in Concentric Jet Experiments as a Function of d

d , cm	$I(729 \text{ cm}^{-1})$	$I(1712, 1718 \text{ cm}^{-1})$	$I(1206 \text{ cm}^{-1})$
0	0.41	0.12	shoulder
-1	0.63	0.29	0.04
-6	0.34	0.20	0.06
-11	0.33	0.12	0.02
-32*	0.23	shoulder	-

*From merged jet length = 32 cm.

Table S2. Key Structural Parameters Calculated^a for the Criegee Intermediate of DMB

parameter ^b	Criegee Intermediate		Acetone
	type	calculated value	calculated value
A(1, 2, 3)	C=O-O	117.77°	-
A(8, 1, 2)	C-C=O	119.53°	121.72°
R(1,2)	C=O	1.267 Å	1.211 Å
R(2, 3)	O-O	1.384 Å	-

^aCalculated at the B3LYP/6-311g(d,2p) level. ^bSee Figure 4b for atom numbering.

Table S3. Calculated^a Bands^b and Intensities^c for the Intermediates Formed in DMB Thermal Reaction with Ozone

Primary Ozonide			Criegee Intermediate			Secondary Ozonide		
freq	¹⁸ O shift	int	freq	¹⁸ O shift	int	freq	¹⁸ O shift	int
20	-1	0	151	0	0	78	-1	2
215	0	0	173	0	1	180	-1	0
244	0	0	274	-8	1	187	-2	0
267	-4	0	305	-8	8	188	0	1
275	-2	0	361	-3	8	225	0	1
283	-1	1	477	-9	0	235	0	0
293	-4	1	596	-17	7	281	-5	4
309	-4	1	811	-11	0	306	0	0
340	-2	1	910	-44	74	354	-11	2
360	-4	1	932	-1	0	367	-6	0
388	-2	1	983	0	8	371	-6	3
449	-13	2	1067	-16	19	453	-9	0
471	-7	4	1089	0	5	509	-11	3
523	-10	4	1306	-1	19	525	-13	19
581	-9	1	1396	-1	33	611	-4	0
647	-7	3	1410	0	5	649	-16	3
689	-27	8	1440	1	7	811	-41	0
760	-40	34	1460	-6	31	827	-31	9
841	-24	4	1473	0	14	848	-20	11
865	-25	14	1480	0	9	854	-17	32
924	-46	3	1557	-15	7	902	-46	0
933	-2	0	3010	8	0	932	0	2
938	-1	1	3023	0	14	935	-3	1
952	-4	4	3058	0	1	966	-2	1
958	-3	6	3065	0	5	1007	-15	113
1017	0	0	3133	0	2	1008	-1	0
1025	-1	0	3135	0	9	1010	-3	7
1160	-2	26				1131	-1	8
1177	-2	17				1223	-4	251
1184	-1	27				1229	-3	53
1224	-1	21				1236	-1	5
1266	-1	2				1258	-2	70
1272	-1	4				1275	0	6
1403	-1	2				1402	0	0
1409	0	24				1403	0	58
1419	0	10				1414	0	28

1430	0	0	1417	0	3
1476	0	1	1479	0	0
1490	0	10	1482	0	0
1491	0	8	1482	0	2
1493	0	5	1483	0	1
1509	0	8	1495	0	1
1512	0	4	1500	0	1
1514	0	14	1502	0	2
1532	0	6	1508	0	14
3035	0	16	3042	0	0
3041	0	9	3042	0	20
3045	0	19	3049	0	23
3050	0	2	3050	-1	1
3094	0	25	3106	0	7
3101	0	9	3106	0	3
3102	0	26	3117	0	6
3109	0	10	3117	0	32
3123	0	13	3126	0	2
3125	0	16	3126	0	24
3132	0	16	3130	0	30
3137	0	16	3130	0	1

^aCalculated at the B3LYP/6-311G++(d,2p) level. ^bFrequencies in cm⁻¹. ^cIntensities in km mol⁻¹.